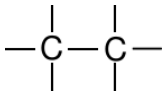
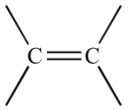
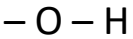
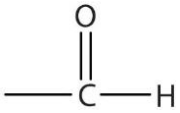
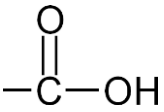
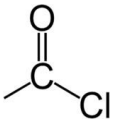
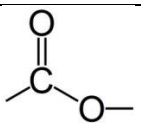
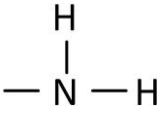
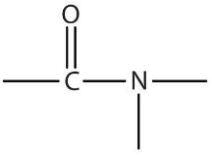
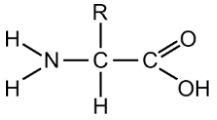
Pearson Edexcel IAL CHEMISTRY

WCH16

REVISION GUIDE

Organic Families

Homologous Series	General formula	Functional group
Alkane	C_nH_{2n+2}	
Alkene	C_nH_{2n}	
Alcohol	$C_nH_{2n+1}OH$	
Halogenoalkane	$C_nH_{2n+1}X$ (X is a halogen)	
Aldehyde	RCHO	
Ketone	RCOR’	
Carboxylic acid	$C_nH_{2n+1}COOH$	
Nitrile	RCN	
Acyl chloride	RCOCl	
Ester	RCOOR’	
Amine	RR’R’’N	
Amide	RCONHR’	
Amino acid	$NH_2CHRCOOH$	

Benzene:

A-) Alkanes

The alkanes are a family of saturated hydrocarbons. They are saturated because they have no double or triple bonds between the carbon atoms, so they contain the maximum amount of hydrogen atoms possible. They are called hydrocarbons because they contain only carbon and hydrogen atoms. All these hydrocarbons have certain properties in common:

- They are insoluble in water.
- They all burn, and in sufficient oxygen they give carbon dioxide and water as the only combustion products.

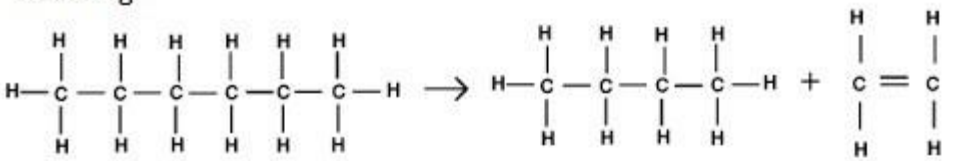
The single most important source of alkanes is crude oil. Alkanes are obtained from fractional distillation, cracking and reformation of crude oil.

- **Reactions of alkanes**

Reaction	Reactants (conditions)	Products
Cracking	Long chain alkane (+ heat/zeolite catalyst)	Alkenes + short-chain/ branched/ cyclic alkanes
Reforming	Straight chain alkane (+ platinum catalyst + heat)	Branched alkanes/arenes (e.g. benzene) + H_2
Combustion: Complete combustion Incomplete combustion	 Sufficient oxygen (+ heat) Insufficient oxygen (+heat)	 $CO_2 + H_2O$ $C + CO + H_2O$
Free radical substitution with chlorine	Alkane + Cl_2 + (UV light)	Halogenoalkane + alkane

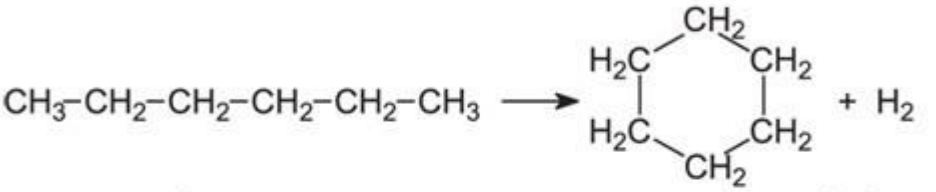
Although alkanes combust well, they are unreactive. The reason for this lack of reactivity is that both C-C and C-H bonds involve a very even sharing of electrons, since the **electronegativities of carbon and hydrogen are very close**. This means that the bonds in the molecules of the alkanes are not polar to any extent, and there are no charges to attract other polar or ionic species. Almost all the reactions of the alkanes occur due to formation of free radicals which contain an unpaired electron.

Cracking



Hexane → Butane + Ethene

Reforming



hexane *cyclohexane* *hydrogen*

Complete combustion

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{energy}$$

Incomplete combustion

$$4CH_4 + 7O_2 \longrightarrow 2CO + 2CO_2 + 8H_2O$$

Free radical substitution with chlorine

Initiation

$$(1)\ Cl_2 \xrightarrow{\text{light}} 2Cl\cdot$$

Propagation

$$(2)\ Cl\cdot + CH_4 \longrightarrow HCl + \cdot CH_3$$

$$(3)\ CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$

Termination

$$(4)\ 2Cl\cdot \longrightarrow Cl_2$$

$$Cl\cdot + \cdot CH_3 \longrightarrow CH_3Cl$$

$$2 \cdot CH_3 \longrightarrow CH_3CH_3$$

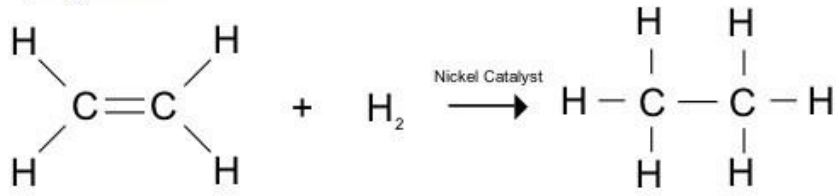
B-) Alkenes

Alkenes are a family of unsaturated hydrocarbons. They are unsaturated because they do not contain the maximum amount of hydrogen possible, since they have at least one C=C double bond.

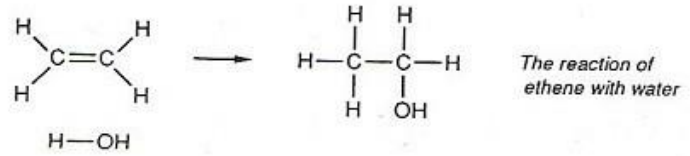
- **Reactions of alkenes**

Addition reactions of alkenes	Reactants (conditions)	Products
Hydrogenation	Alkene + H_2 (+ Nickel + 150°C)	Alkane
Addition of water	Alkene + H_2O **(g)**	Alcohol
Addition of halogens	Alkene + Br_2	Halogenoalkane (Brown to colourless)
Addition of hydrogen halides	Alkene + HBr	Halogenoalkane
Oxidation by potassium manganate(VII)	Alkene + $KMnO_4$ (+ dil H_2SO_4)	Diol
Addition polymerisation	Alkene (+ catalyst)	Addition polymer

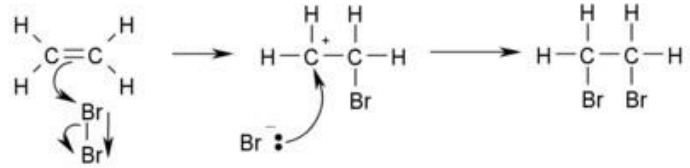
Hydrogenation



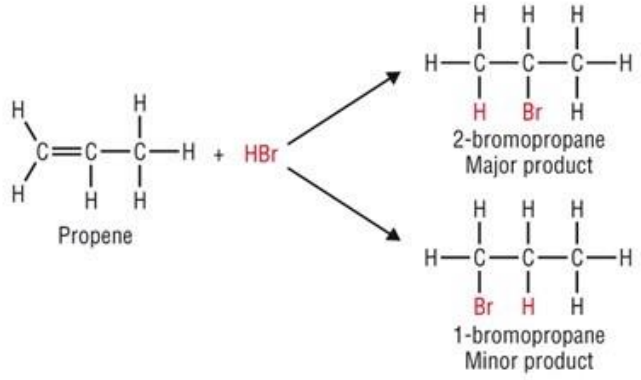
Addition of water



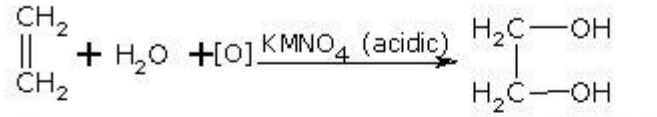
Addition of halogens



Addition of hydrogen halides

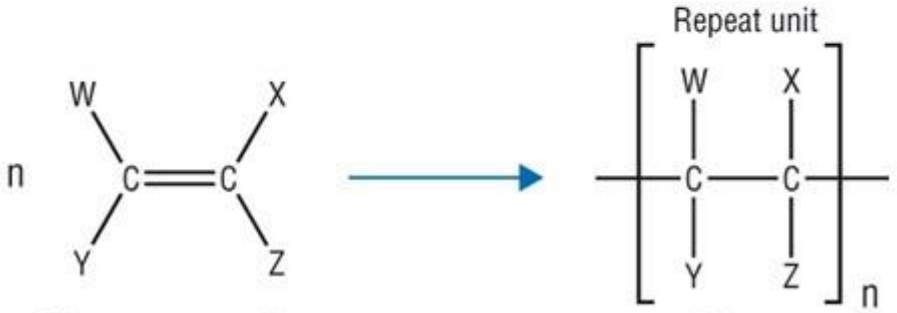


Oxidation by potassium manganate(VII)



ethane ethane-1.2-diol

Addition polymerisation



Monomer – any alkene Polymer

C-) Alcohols

Alcohols have one of three types of structure – they may be primary, secondary or tertiary.

- Primary alcohols have the general structure RCH_2OH. This means there are two hydrogen atoms attracted to the carbon joined to the –OH group.
- Secondary alcohols have two alkyl groups and one hydrogen atom attracted to the carbon that is joined to the –OH group, giving them the general structure RR_1CHOH.
- Tertiary alcohols have three alkyl groups and no hydrogen atoms attached to the carbon that is joined to the –OH group, so they have the general structure RR_1R_2COH.

- **Reactions of alcohols**

Reaction	Reactants (conditions)	Products
Combustion	Alcohol + O_2	CO_2 + H_2O
Reaction with sodium	Alcohol + Na	Salt + H_2
Reaction with PCl_5	Alcohol + PCl_5	Chloroalkane + $POCl_3$ + HCl
Oxidation of primary alcohols Partial oxidation Complete oxidation	 Alcohol + $K_2Cr_2O_7$ + H_2SO_4 (distillation) Alcohol + $K_2Cr_2O_7$ + H_2SO_4 (reflux)	 Aldehyde + … Carboxylic acid + …
Oxidation of secondary alcohols	Alcohol + $K_2Cr_2O_7$ + H_2SO_4 (reflux-distillation)	Ketone

Combustion

$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

Reaction with sodium

$2Na(s) + 2CH_3CH_2OH(l) \rightarrow 2CH_3CH_2O^-Na^+(alc) + H_2(g)$

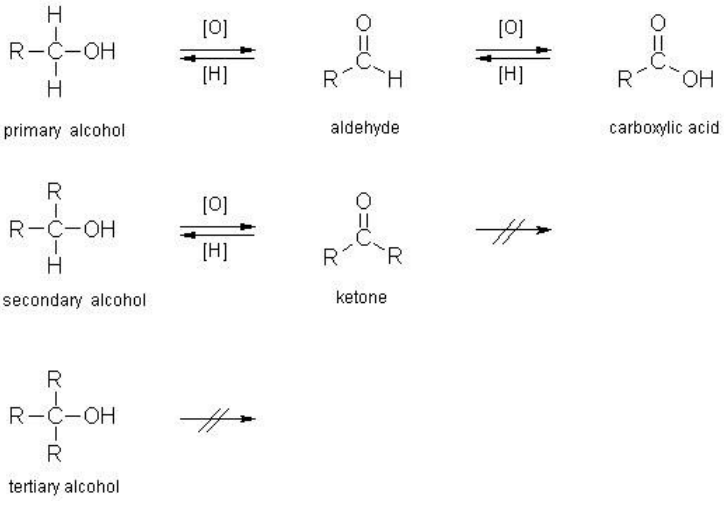
sodium ethoxide (dissolved in ethanol)

Reaction with PCl_5

$CH_3CH_2OH(l) + PCl_5(s) \rightarrow CH_3CH_2Cl(l) + POCl_3(l) + HCl(g)$

chloroethane

Oxidation of alcohols



Preparing halogenoalkanes from alcohols

1. Preparing a bromoalkane from a primary alcohol

A. Introduction

The aim of this experiment is to synthesise a pure sample of 1-bromobutane from butan-1-ol. The alcohol reacts with hydrogen bromide formed from sodium bromide and 50% sulfuric acid.

B. Safety

Possible hazards

- Sulfuric acid is corrosive.
- The bromine which forms during the reaction is corrosive and toxic.
- Butan-1-ol is a flammable liquid.
- Heating a liquid in a small flask can lead to bumping. Bumping is violent boiling which shakes the apparatus and can eject liquid from the container in which it is being heated.
- Pressure can build up in a tap funnel when gases are evolved.

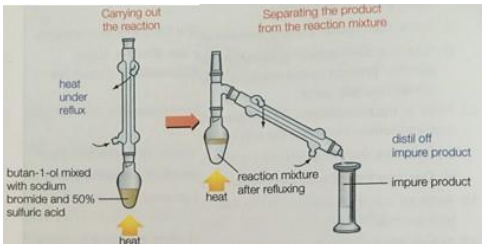
Precautions

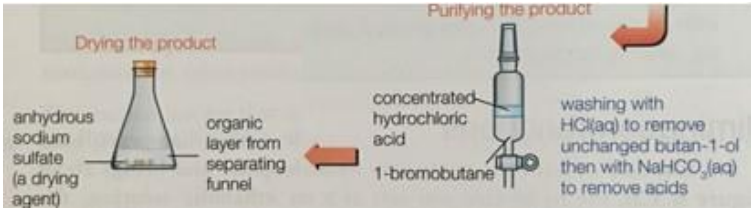
- Wear eye protection.
- Carry out the heating under reflux in a fume cupboard.
- Heat with an electrical heater instead of a flame.
- Release the pressure in the tap funnel by inverting it and opening the tap from time to time.

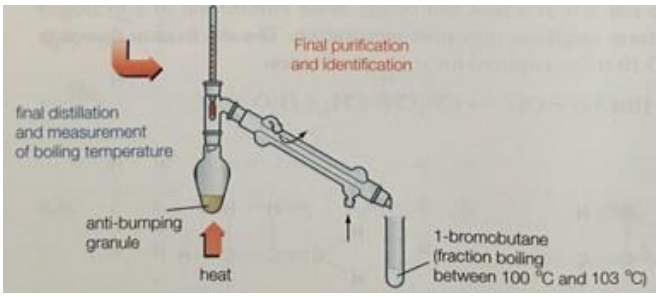
Note: Concentrated sulfuric acid is not used because it would rapidly oxidise bromide ions or hydrogen bromide to bromine and lead to liberation of toxic bromine.

Note: The reflux condenser prevents the loss of volatile liquids from the reaction mixture during heating.

C. Apparatus




Drying the product
Purifying the product
anhydrous sodium sulfate (a drying agent)
organic layer from separating funnel
concentrated hydrochloric acid
1-bromobutane
washing with HCl(aq) to remove unchanged butan-1-ol then with NaHCO3(aq) to remove acids



D. PROCEDURE

- Butan-1-ol is mixed with sodium bromide and 50% sulfuric acid.

$H_2SO_4 + NaBr \rightarrow KHSO_4 + HBr$

$CH_3CH_2CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2CH_2Br + H_2O$

- The mixture is heated under reflux.
- The condenser is rearranged for separating the product. Impure product is distilled off.
- The product left in the round-bottom flask is washed with HCl(aq) to remove unchanged butan-1-ol then with $NaHCO_3$(aq) to remove acids. Aqueous sodium hydrogencarbonate is a weak alkali which neutralises acids without hydrolysing the product. Strong alkalis would hydrolyse halogenoalkanes.
- Organic layer is separated from the aqueous layer using a separating funnel.

Organic layer	Aqueous layer
Unreacted butan-1-ol	Unreacted butan-1-ol
Bromine	Oxides of sulfur
But-1-ene	Hydrogen bromide
	Water

table 2.8.5 Impurities that may be in 1-bromobutane prepared from an alcohol.

- Anhydrous sodium sulfate is added to dry the product. Anhydrous sodium sulfate is a **drying agent**.
- Finally, pure 1-bromobutane is separated from the previous mixture by distillation.
- For identification, the boiling temperature of 1-bromobutane is checked. (100°C-103°C).

The percentage yield of this reaction is not 100% because:

- Some unchanged butan-1-ol remains in this preparation even with an excess of sodium bromide and concentrated sulfuric acid.
- Some of the butan-1-ol is converted to by-products.
- Some of the product is lost during the process as the chemicals are mixed, heated, distilled, transferred from one container to another, washed, dried and redistilled.

2. Preparing an iodoalkane from a primary alcohol

Procedure

1. Suitable quantities of red phosphorus and butan-1-ol are placed in a round-bottomed flask fitted with a reflux condenser.
2. The mixture is heated until it boils gently and then the heat source is removed.
3. A suitable quantity of powdered iodine is added in small portions down the condenser at a rate which just maintains gentle boiling. The reaction should be allowed to subside after each addition.
4. After the addition of iodine is complete, the mixture is heated under reflux for 30 – 60 minutes, until little or no iodine is visible.
5. The apparatus is allowed to cool and the condenser rearranged for distillation.
6. The crude 1-iodobutane is distilled off until the residue in the distilling flask is about one-fifth of its original volume. Double its volume of water is added and the distillation continued until no more oily drops condense into the receiver.
7. The crude 1-iodobutane is separated and washed with dilute sodium thiosulfate solution and then with dilute sodium carbonate solution.
8. The organic layer is separated and allowed to stand over anhydrous calcium chloride.

Reactions:

Iodine reacts with the red allotrope of phosphorus to form phosphorus triiodide:

$2P + 3I_2 \rightarrow 2PI_3$

Phosphorus triiodide then reacts with water to form hydrogen iodide gas:

$PI_3 + 3H_2O \rightarrow 3HI + H_3PO_4$

This is how gaseous hydrogen iodide is prepared. Hydrogen iodide, then, reacts with butan-1-ol to produce the iodoalkane.

Note: A metal halide and concentrated sulfuric acid should not be used when making a bromoalkane or iodoalkane.

- ➔ Little or no hydrogen bromide/iodide would be produced on the addition of the metal halide to concentrated sulfuric acid as bromide/iodide ions would be quickly oxidised to bromine/iodine. Toxic bromine/iodine gas would be liberated and since little or no hydrogen bromide/iodide is produced, halogenoalkane cannot be produced.

D-) Halogenoalkanes

Halogenoalkanes are a family of chemicals that are found relatively rarely in the natural world. A halogenoalkane has a hydrocarbon skeleton with a halogen functional group. It is formed when a halogen atom replaces a hydrogen atom in a hydrocarbon molecule. The properties of an organic halogen are affected by three things:

- The type of hydrocarbon skeleton
- The halogen or halogens attached
- The position of the halogen in the molecule

Changing the position of a halogen atom within a halogenoalkane makes a great difference to the properties of the molecule.

- Primary halogenoalkanes have two hydrogen atoms bonded to the carbon atom carrying the halogen.
- Secondary halogenoalkanes have one hydrogen atom bonded to the carbon atom carrying the halogen. The halogen-carrying carbon is bonded to two other carbon atoms.
- Tertiary halogenoalkanes have no hydrogen atoms bonded to the carbon carrying the halogen. This carbon atom is bonded to three other carbon atoms.

• Physical properties of halogenoalkanes

Chloromethane, bromoethane and chloroethane are gases at room temperature. Iodomethane and the rest of the homologous series are liquid. The boiling temperatures of halogenoalkanes are higher than those of alkanes, primarily because halogenoalkanes contain more electrons and so have stronger London forces. In addition, because the molecules are polar, there are permanent dipole-dipole forces between the molecules which strengthen the intermolecular forces and so increase the boiling temperature.

Even though they are polar molecules, they are insoluble in water because they cannot form hydrogen bonds.

• Reactions of halogenoalkanes

Reaction	Reactants (conditions)	Products
Reaction with aqueous alkali	Halogenoalkane + KOH (aq)	Alcohol
Reaction with alcoholic alkali	Halogenoalkane + KOH (alc)	Alkene
Reaction with alcoholic ammonia	Halogenoalkane + NH_3 (alc)	Amines
Reaction with $AgNO_3$(aq)	Halogenoalkane + $AgNO_3$ (aq)	Coloured precipitates

Reaction with aqueous alkali

$$RX + OH^- \rightarrow ROH + X^-$$

Reaction with alcoholic alkali

$$CH_3CHBrCH_3 + OH^- \rightarrow CH_3CH{=}CH_2 + H_2O + Br^-$$

2-bromopropane + hydroxide ions → propene + water + bromide ions

Reaction with alcoholic ammonia

$$CH_3CH_2I + NH_3 \rightarrow CH_3CH_2NH_2 + HI$$

iodoethane → ethylamine

This is not the end of the story, however. Ethylamine possesses a lone pair of electrons, just like ammonia. It reacts further with iodoethane:

$$CH_3CH_2NH_2 + CH_3CH_2I \rightarrow (CH_3CH_2)_2NH + HI$$

ethylamine + iodoethane → diethylamine

In turn, there are two further stages:

$$(CH_3CH_2)_2NH + CH_3CH_2I \rightarrow (CH_3CH_2)_3N + HI$$

diethylamine + iodoethane → triethylamine

$$(CH_3CH_2)_3N + CH_3CH_2I \rightarrow (CH_3CH_2)_4N^+I^-$$

triethylamine + iodoethane → tetraethylammonium iodide

Reaction with $AgNO_3(aq)$

Halide	Silver nitrate	Effect of sunlight	Ammonia solution
Chloride	White precipitate	White precipitate turns purple-grey	Precipitate dissolves.
Bromide	Cream precipitate	Cream precipitate turns green-yellow	In dilute ammonia, precipitate partially dissolves. In concentrated ammonia precipitate dissolves.
Iodide	Yellow precipitate	No effect	Precipitate does not dissolve.

E-) Aldehydes

In aldehydes, the **carbonyl carbon has a hydrogen atom attached to it**, together with either a second hydrogen atom, or, much more commonly a hydrocarbon group, which might be an alkyl group or one containing a benzene ring. Aldehydes can be produced by the oxidation of primary alcohols.

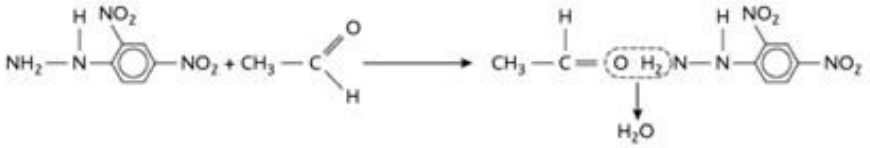
- **Physical properties**

Boiling temperature	Solubility in water
➔ Relatively high boiling T The carbonyl group cannot take part in hydrogen bonding, but there are permanent dipole-dipole interactions between aldehyde molecules and between ketone molecules. This gives them boiling temperatures which are higher than those of the corresponding alkanes, but lower than those of the corresponding alcohols. Molecules of straight-chain isomers can pack closer together than those of branched-chain molecules. This means that the forces between molecules of straight-chain isomers are stronger than those between molecules of branched-chain isomers – so the boiling temperatures of straight-chain isomers are higher.	➔ Small molecules soluble Aldehydes and ketones composed of small molecules are miscible with water in all proportions, but this decreases with increasing chain length. The reason for the solubility is that they can form hydrogen bonds with water molecules even though they cannot form hydrogen bonds with themselves. With its δ+ charge, one of the water molecule's hydrogen atoms can be sufficiently attracted to one of the lone pairs on the oxygen atom of a carbonyl group for a hydrogen bond to be formed. Dispersion forces and dipole-dipole attractions between the aldehyde or ketone and the water molecules will also exist.

- **Reactions of aldehydes**

Reactants	Product	Reaction (+ mechanism)
Aldehyde + 2,4-dinitrophenylhydrazine	2,4-DNPH derivative Yellow-red solid	Condensation reaction
Aldehyde + oxidation by: Fehling's or Benedict's solution Acidified sodium dichromate(VI) Tollens' reagent	Carboxylic acid (blue to red) (orange to green) (silver mirror)	Oxidation reaction
Aldehyde + reduction by: Lithium aluminium hydride + dry ether	Primary alcohol	Reduction reaction
Aldehyde + hydrogen cyanide	Nitrile	Nucleophilic addition***

2,4-dinitrophenylhydrazine



2,4-dinitrophenylhydrazine ethanal ethanal 2,4-dinitrophenylhydrazone

Fehling's and Benedict's solution

$$2Cu^{2+}(aq) + OH^-(aq) + 2e^- \rightarrow Cu_2O(s) + H^+(aq)$$

$$RCHO(aq) + H_2O(l) \rightarrow RCOOH(aq) + 2H^+(aq) + 2e^-$$

so overall:

$$2Cu^{2+}(aq) + RCHO(aq) + OH^-(aq) + H_2O(l) \rightarrow Cu_2O(s) + RCOOH(aq) + 3H^+(aq)$$

Acidified sodium dichromate(VI)

$$3CH_3CHO(l) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3COOH(aq) + 4H_2O(l) + 2Cr^{3+}(aq)$$

ethanal — ethanoic acid

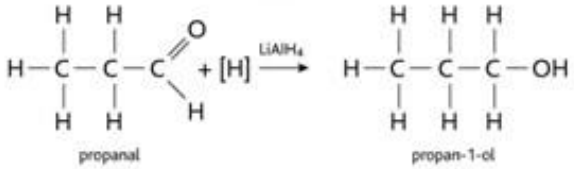
Tollens' reagent

The half reactions are:

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

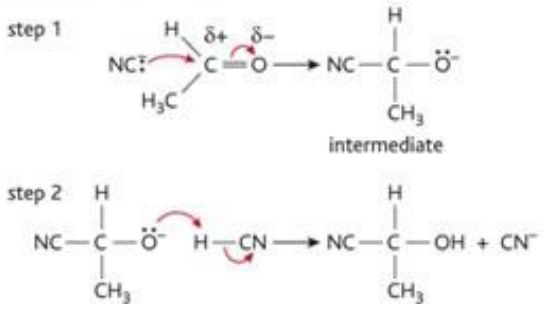
$$RCHO(aq) + H_2O(l) \rightarrow RCOOH(aq) + 2H^+(aq) + 2e^-$$

Lithium aluminium hydride dissolved in ethoxyethane (dry ether)



propanal propan-1-ol

Hydrogen cyanide



intermediate

F-) Ketones

In ketones, the **carbonyl group has two hydrocarbon groups** attached. Again these can be either alkyl groups or groups containing benzene rings. Ketones can be produced by the oxidation of secondary alcohols.

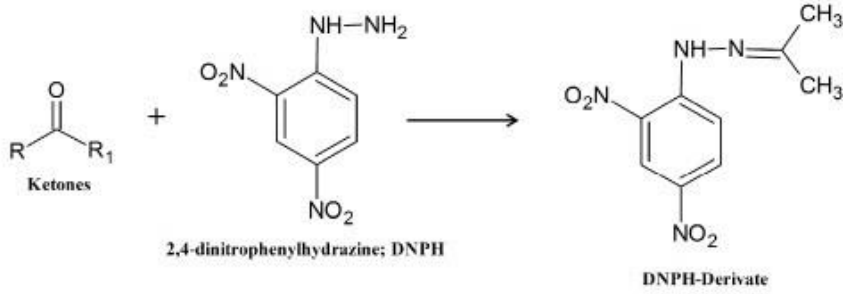
- **Physical properties**

Boiling temperature	Solubility in water
➔ Relatively high boiling T The carbonyl group cannot take part in hydrogen bonding, but there are permanent dipole-dipole interactions between aldehyde molecules and between ketone molecules. This gives them boiling temperatures which are higher than those of the corresponding alkanes, but lower than those of the corresponding alcohols. Molecules of straight-chain isomers can pack closer together than those of branched-chain molecules. This means that the forces between molecules of straight-chain isomers are stronger than those between molecules of branched-chain isomers – so the boiling temperatures of straight-chain isomers are higher.	➔ Small molecules soluble Aldehydes and ketones composed of small molecules are miscible with water in all proportions, but this decreases with increasing chain length. The reason for the solubility is that they can form hydrogen bonds with water molecules even though they cannot form hydrogen bonds with themselves. With its δ+ charge, one of the water molecule's hydrogen atoms can be sufficiently attracted to one of the lone pairs on the oxygen atom of a carbonyl group for a hydrogen bond to be formed. Dispersion forces and dipole-dipole attractions between the aldehyde or ketone and the water molecules will also exist.

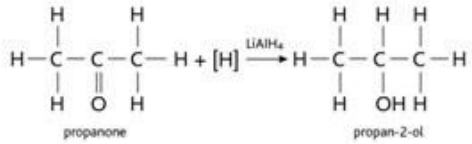
- **Reactions of ketones**

Reactants	Product	Reaction (+ mechanism)
Ketone + 2,4-dinitrophenylhydrazine	2,4-DNPH derivative Yellow-red solid	Condensation reaction
Ketone + reduction by: Lithium aluminium hydride + dry ether	Secondary alcohol	Reduction reaction
Ketone + hydrogen cyanide	Nitrile	Nucleophilic addition***

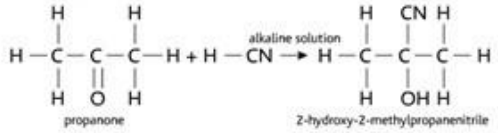
2,4-dinitrophenylhydrazine



Lithium aluminium hydride +dry ether

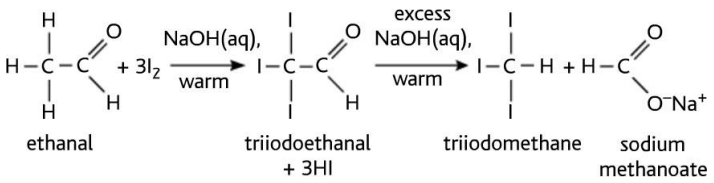


Hydrogen cyanide



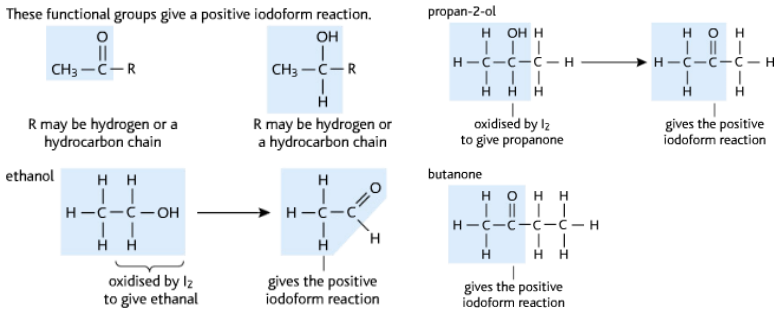
Carbonyl compounds and iodine (Iodoform reaction)

When ethanal is warmed with **iodine** in alkaline solution, a two-stage reaction takes place.



First, the aldehyde reacts with the iodine to form triiodoethanal; and then this reacts with the alkali to form triiodomethane. Triiodomethane (or iodoform) is an insoluble yellow solid with a characteristic smell. It forms a precipitate.

This iodoform reaction is specific to organic compounds that contain a methyl group next to a carbonyl group or can react to give a methyl group next to a carbonyl group.


These functional groups give a positive iodoform reaction.
R may be hydrogen or a hydrocarbon chain
R may be hydrogen or a hydrocarbon chain
propan-2-ol
oxidised by I2 to give propanone
gives the positive iodoform reaction
ethanol
oxidised by I2 to give ethanal
gives the positive iodoform reaction
butanone
gives the positive iodoform reaction

G-) Carboxylic acids

Carboxylic acids contain the carboxyl group. This is a complex functional group which is made up of a hydroxyl group –OH and a carbonyl group C=O. These two functional groups are so close together they affect each other. Because of this, the reactions of the carboxylic acids tend to differ from those of the corresponding alcohols, aldehydes and ketones.

The properties of the carboxylic acids, both physical and chemical, are largely governed by two factors:

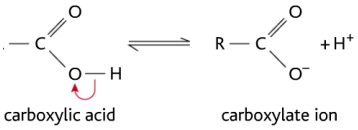
— The polarity of the carboxyl group
— The length of the carbon chain

- **Physical properties**

Boiling temperature	Solubility in water
➔ High boiling temperatures The presence of two polarised groups means that carboxylic acid molecules experience relatively strong intermolecular forces. So they have relatively high melting and boiling temperatures. Furthermore, the polarity and structure of the molecules is such that they can exist as hydrogen-bonded dimmers in all states.	➔ High solubility in water Hydrogen bonding is also responsible for the high solubility of the smaller carboxylic acid molecules in water and other polar solvents. Longer-chained acids become less soluble because the organic nature of the carbon chain becomes dominant.

Acidic properties of carboxylic acids

When a carboxylic acid is dissolved in water, it dissociates forming hydrogen ions and carboxylate ions, so behaving as an acid. Although the carboxylate ion is drawn with one double bond, X-ray diffraction analysis and observations of the ways in which it reacts suggest that the two carbon-oxygen bonds are actually identical. This implies that the negative charge is delocalised over the whole of the carboxylate group, which means that it will not attract positively charged particles as strongly as might be expected. The carboxylic acids are relatively strong acids and the carboxylate ion is a relatively weak base.



g. 1.6.42 The dissociation of a carboxylic acid.

- **Reactions of carboxylic acids**

Reaction	Reactants (conditions)	Products
Oxidation of primary alcohols or aldehydes	Conc H_2SO_4 + $Na_2Cr_2O_7$ Heat under reflux	Carboxylic acids + H_2O
Hydrolysis of a nitrile	Boil with dilute H_2SO_4	Carboxylic acids + NH^+_4
Reduction of carboxylic acids	$LiAlH_4$ in dry ether	Primary alcohols
Reaction with phosphorus(V) chloride	Phosphorus(V) chloride	Acyl chloride + $POCl_3$ + HCl
Neutralisation of carboxylic acids	A base	Salt + H_2O
Esterification reaction	Alcohol + H_2SO_4	Ester + H_2O

Oxidation of primary alcohols and aldehydes

$$\underset{\text{ethanol}}{CH_3CH_2OH(l)} + 2[O] \rightarrow \underset{\text{ethanoic acid}}{CH_3COOH(aq)} + H_2O(l)$$

Hydrolysis of a nitrile

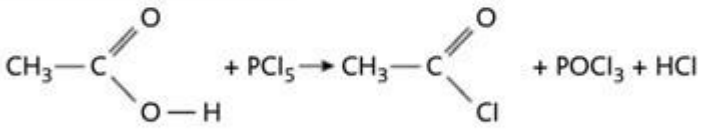
$$\underset{\text{propanenitrile}}{CH_3CH_2CN(l)} + 2H_2O(l) + H^+(aq) \rightarrow \underset{\text{propanoic acid}}{CH_3CH_2COOH(aq)} + NH_4^+(aq)$$

Lithium aluminium hydride in dry ether

$$CH_3CH_2COOH(l) + 2[H] \rightarrow CH_3CH_2CH_2OH(l) + H_2O(l)$$

Addition of water at the end of the reaction will destroy any excess lithium tetrahydridoaluminate.

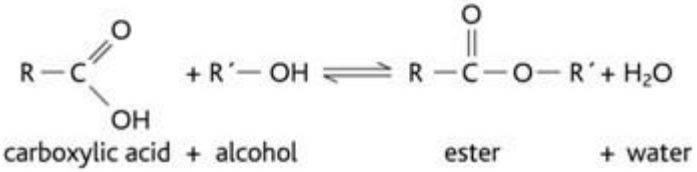
Phosphorus(V) chloride



A base (Sodium hydroxide)

$$CH_3COOH(aq) + NaOH(aq) \rightleftharpoons CH_3COO^-(aq) + Na^+(aq) + H_2O(l)$$

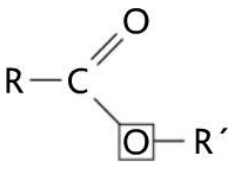
Alcohol



H-) Esters

Esters are volatile compounds. They do not form hydrogen bonds and so their melting and boiling temperatures are relatively low and they are not soluble in water or other polar solvents.

A distinct feature of an ester molecule is the oxygen atom which forms a bridge between the two parts. This oxygen bridge is formed as the carboxylic acid and alcohol molecules join. It was shown using radioactive O-18 atom that the **bridging oxygen in the ester comes from the alcohol molecule and not the carboxylic acid**.

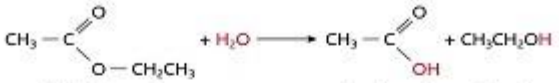


- **Reactions of esters**

Reaction	Reactants (conditions)	Products
Acid hydrolysis	Dilute acid + boil (reflux)	Carboxylic acid + alcohol
Base hydrolysis	Alkali solution + boil (reflux)	Carboxylate ion + alcohol
Trans-esterification	Alcohol	Trans ester
Polymerisation	A diol (alcohol with 2 OH groups)	Polyester

Acid hydrolysis

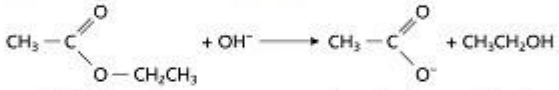
Esters can be split up by boiling with water and, much more effectively, by using a dilute acid. The dilute acid provides hydrogen ions, which catalyse the reaction.



ethyl ethanoate — ethanoic acid — ethanol

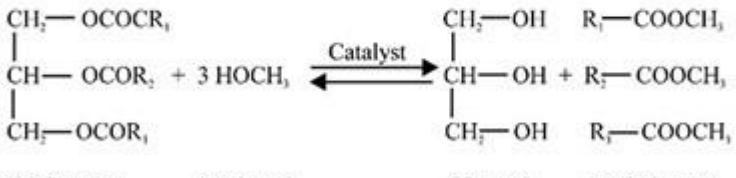
Base hydrolysis

An ester can also be hydrolysed by boiling it with alkali solution, such as NaOH. This is a more efficient process because when the acid is released it is neutralised by alkali to form the sodium salt. This does not react with the alcohol.



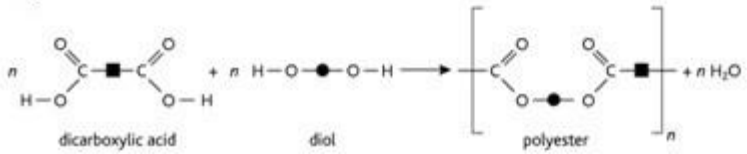
ethyl ethanoate — ethanoate ion — ethanol

Trans-esterification



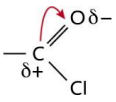
Triglyceride (parect oil) — Methanol (alcohol) — Glycerol — Methyl esters (biodiesel)

Polymerisation

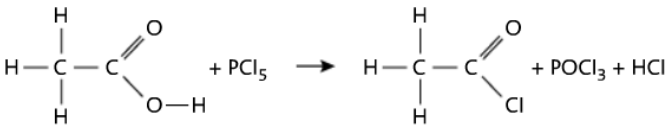


dicarboxylic acid — diol — polyester

I-) Acyl chlorides



Acyl chloride are reactive compound produced when phosphorus(V) chloride reacts with a carboxylic acid. Acyl chlorides contain a carbonyl group with a chlorine atom attached to the carbon atom in the carbonyl group. The oxygen in the carbonyl group withdraws electrons from the double bond, giving the central carbon atom a $\delta+$ charge – making it susceptible to attack by nucleophiles.

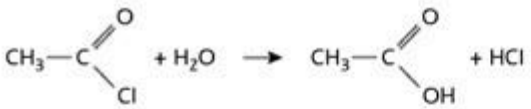


ethanoic acid — ethanoyl chloride

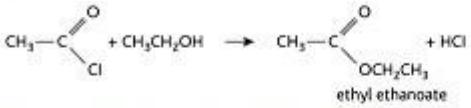
- **Reactions of acyl chlorides**

Reactants	Products	Reaction (+ mechanism)
Cold water	Carboxylic acid + HCl (white fumes)	Hydrolysis
Alcohols	Ester + HCl (white fumes)	Nucleophilic addition
Concentrated ammonia	Amides + HCl (white fumes)	Nucleophilic addition
Amines	N-substituted amide + HCl (white fumes)	Nucleophilic addition

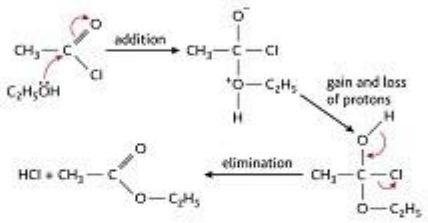
Cold water



Alcohols



Mechanism for this nucleophilic addition/elimination reaction



Concentrated ammonia

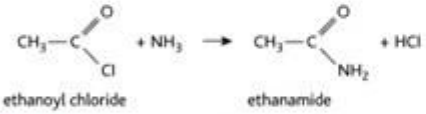
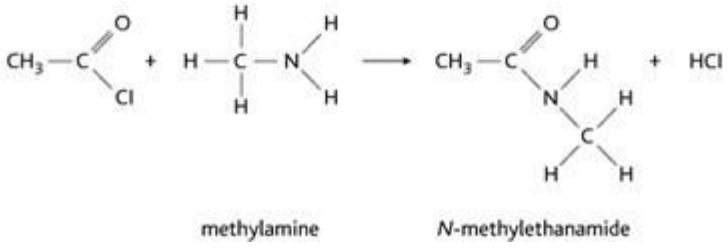


fig. 1.6.75 Reaction of acyl chlorides with ammonia.

Because of the acid/base nature of the products, a further reaction takes place:

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

Amines



J-) Benzene

The arrangement of the electrons in benzene is very different. Each carbon atom forms a single sigma bond with each of the two carbon atoms joined to it. This forms the skeleton of the molecule, giving a planar hexagonal ring.

Each carbon atom has one p orbital containing a single electron, and it is the lobes of these p orbitals that fuse to form a single ring of charge above and another single ring below the sigma-bonded skeleton. Within these extended pi bonds, the electrons are free to move around the ring – they are localised. It is this delocalisation that causes all the carbon-carbon bonds in benzene to be identical, and which also makes the benzene molecule so unexpectedly stable.

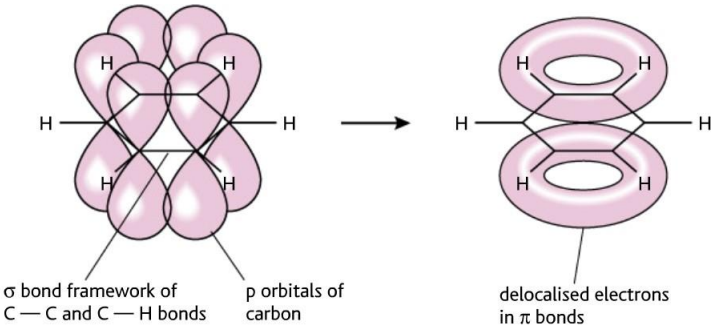


fig. 2.3.13 The delocalisation of the electrons in the π bonds of the symmetrical six-membered ring structure of benzene explains why the chemical and physical properties of benzene are so different from those of straight-chain compounds containing double bonds.

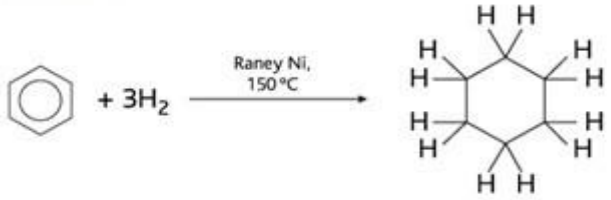
- **Reactions of benzene**

Reactants (+ condition)	Product(s)	Reaction (+ mechanism)
Oxygen (+ burn)	$CO_2 + H_2O$ (yellow flame + smoky)	Combustion
H_2 (+ Nickel catalyst + 150° C)	Cyclohexane	Hydrogenation
Bromine (+ UV)	1,2,3,4,5,6-hexabromocyclohexane	Free radical addition
Fuming H_2SO_4 (+ reflux)	Benzenesulfonic acid	Sulfonation – electrophilic substitution
Halogens (+ halogen carrier)	Halogenobenzene	Halogenation – electrophilic substitution
Conc $HNO_3 + H_2SO_4$ **(+ <50°C)**	Nitrobenzene	Nitration – electrophilic substitution
Halogenoalkane (+ halogen carrier)	Alkylbenzene (Alkane)	Alkylation – electrophilic substitution
Acyl chloride (+ halogen carrier)	Phenylketone (Ketone)	Acylation – electrophilic substitution

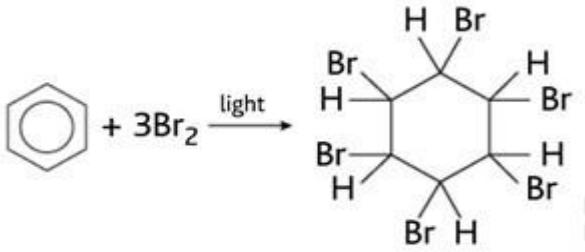
Oxygen

$$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$$

Hydrogen

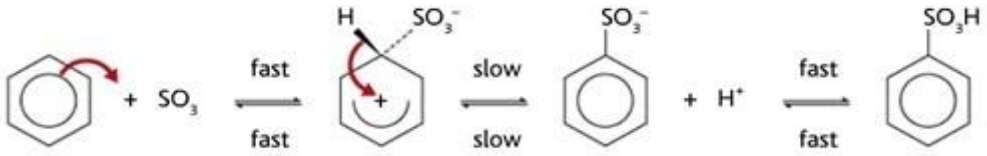


Bromine (UV)



1,2,3,4,5,6-hexabromocyclo-hexane

Fuming H_2SO_4



Halogens (+ halogen carrier)

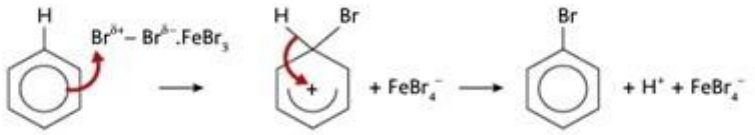
Iron can be used instead of iron(III) bromide because iron reacts with some of the bromine present to form iron(III) bromide:

$$2Fe(s) + 3Br_2(l) \rightarrow 2FeBr_3(s)$$

The iron(III) bromide polarises the bromine molecule, forming a complex:

$$\overset{\delta+\quad\delta-}{Br—Br} + FeBr_3 \rightarrow Br—Br.FeBr_3$$

This acts as an electrophile, forming first a weak π complex, and then the more stable σ complex:

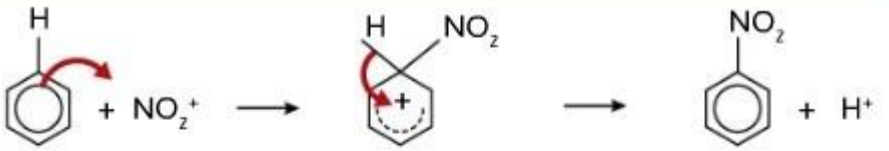


A proton is then lost and this reacts to regenerate the iron(III) bromide, forming HBr:

$$H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$$

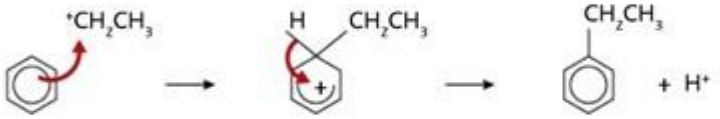
Conc $HNO_3 + H_2SO_4$

$$HNO_3(l) + 2H_2SO_4(l) \rightleftharpoons NO_2^+(sol) + 2HSO_4^-(sol) + H_3O^+(sol)$$



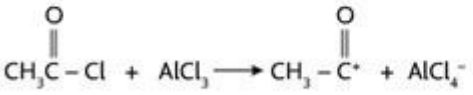
Halogenoalkane (+ halogen carrier)

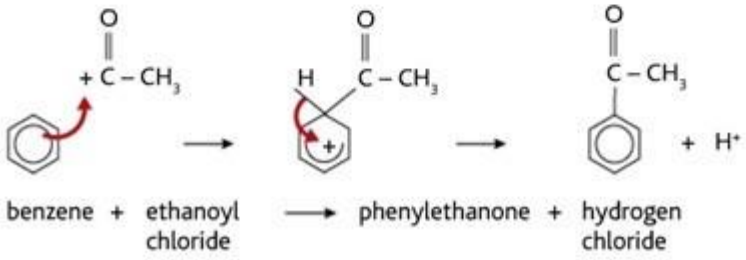
$$CH_3CH_2Cl + AlCl_3 \longrightarrow CH_3CH_2^+ + AlCl_4^-$$



$$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$$

Acyl chloride (+ halogen carrier)





benzene + ethanoyl chloride → phenylethanone + hydrogen chloride

$$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$$

➔ Phenol

Preparation of phenol from benzene

- Benzene undergoes nitration reaction. It is reacted with concentrated sulfuric acid and concentrated nitric acid. The product is nitrobenzene.
- Nitrobenzene undergoes side-chain reduction to phenylamine by reflux using tin and concentrated hydrochloric acid.
- Diazotization to benzenediazonium chloride takes place using nitrous acid (sodium nitrite and hydrochloric acid) below 10°C.
- The product is converted to phenol by boiling with dilute sulfuric acid – hydrolysis reaction with substitution of diazo group by OH.

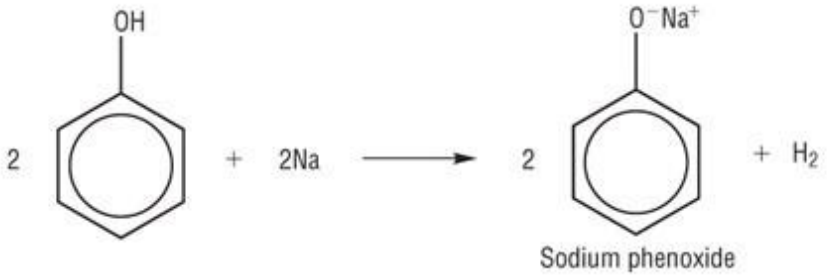
- **Reactions of phenol**

Reaction	Products	
Combustion of phenol	$CO_2 + H_2O$	
Reaction with sodium	Sodium phenoxide + H_2	
Reaction with bromine water	2,4,6-tribromophenol + HBr	Multi-electrophilic substitution Bromine water decolourised
Reaction with dilute nitric acid	2,4,6-trinitrophenol + H_2O	Multi-electrophilic substitution

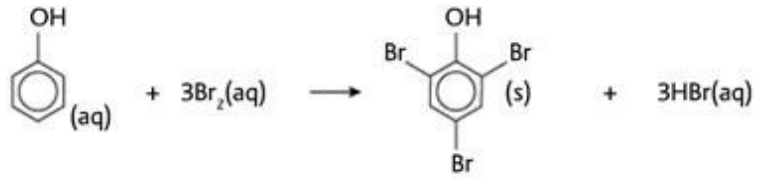
Combustion of phenol

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O$$

Reaction with sodium



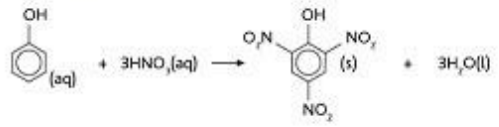
Reaction with bromine water



phenol bromine solution 2,4,6-tribromophenol hydrogen bromide

Reaction with dilute nitric acid

When dilute nitric acid is added to a solution of phenol, a white precipitate of 2,4,6-trinitrophenol is formed. Again this is a multiple substitution reaction. Compared to benzene, phenol does not need sulfuric acid to assist nitration and the nitric acid is dilute. The substitution happen in the 2,4 and 6 positions of the ring.



phenol nitric acid 2,4,6-trinitrophenol water

K-) Amines

The **amines are organic compounds based on ammonia**, where one or more of the three hydrogen atoms have been substituted by an alkyl or aryl group. The number of these groups determines whether the compound is a primary amine, a secondary amine or a tertiary amine.

- If one hydrogen atom has been replaced, then it is a primary amine.
- If two hydrogen atoms have been replaced, then it is a secondary amine.
- If three hydrogen atoms have been replaced, then it is a tertiary amine.

- **Physical properties of amines**

— Like ammonia, the amines have unpleasant smells – some resemble a fishy smell.

— Like ammonia, the aqueous solutions are alkaline.

— The hydrocarbon part of the molecule is hydrophobic but the amine group is able to hydrogen-bond both to itself and water. The amine group is hydrophilic. The larger the hydrophilic group, the lower the solubility of amine in water.

Phenylamine, with its large non-polar benzene ring, is only slightly soluble in water. Tertiary amines are also not soluble because hydrogen bonding is not possible and the interactions between molecules are only van der Waals forces.

Amines as Bronsted-Lowry bases

- **Butylamine**

Butylamine and other amines act as Bronsted-Lowry bases in a similar manner by removing H^+ ions from water molecules to form an alkaline solution containing hydroxide ions.

$$C_4H_9NH_2\ (aq) + H_2O\ (aq) \rightleftharpoons C_4H_9NH_3^+(aq) + OH^-\ (aq)$$

As with ammonia, the reaction of amines with water is reversible so alkyl amines are also weak bases, although stronger than ammonia. This is because the alkyl group is electron releasing and increases the electron density on the lone pair on the nitrogen. This effect makes the lone pair more attractive to protons than the lone pair on the nitrogen in ammonia. The equilibrium lies further to the right than the equilibrium involving ammonia.

- **Phenylamine**

By contrast, phenylamine is a much weaker base than ammonia because the lone pair in phenylamine is delocalised into the π cloud of the benzene ring and is less attractive to protons than the lone pair in ammonia. Therefore, the equilibrium for the reaction of phenylamine with water lies further to the left than that for ammonia.

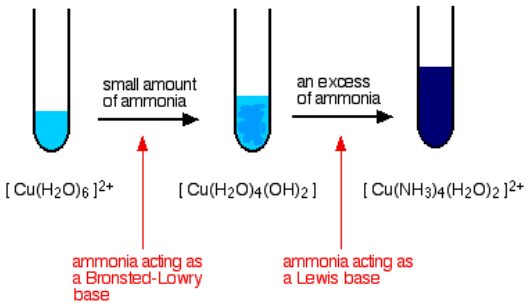
$$C_6H_5NH_2\ (l) + H_2O\ (l) \rightleftharpoons C_6H_5NH_3^+\ (aq) + OH^-\ (aq)$$

If a strong base, such as sodium hydroxide, is added to the aqueous phenylammonium ions, H^+ ions are removed from the phenylammonium ions and yellow, oily phenylamine reforms.

$$C_6H_5NH_3^+ (aq) + OH^- (aq) \rightarrow C_6H_5NH_2 (l) + H_2O (l)$$

Amines as ligands

When ammonia and amines act as bases and accept a proton, they do so by donating a lone pair of electrons to the proton. Ammonia and amines can also donate a lone pair of electrons to transition metal ions and act as ligands.


small amount of ammonia
an excess of ammonia
[Cu(H2O)6]2+
[Cu(H2O)4(OH)2]
[Cu(NH3)4(H2O)2]2+
ammonia acting as a Bronsted-Lowry base
ammonia acting as a Lewis base

When butylamine is added to aqueous copper(II) sulfate solution, a deep blue solution is formed. Four butylamine molecules replace four water ligands and a deep blue complex is formed.

$$4C_4H_9NH_2 (aq) + [Cu(H_2O)_6]^{2+} (aq) \rightarrow [Cu(C_4H_9NH_2)_4(H_2O)_2]^{2+} (aq) + 4H_2O (l)$$

- **Reactions of amines**

Reaction	Reactants (conditions)	Products
Preparation of amines: Hydrogenation of nitriles Reduction of nitriles Reaction of NH_3 and halogenoalkanes	 Nitrile + H_2 + Nickel catalyst Nitrile + $LiAlH_4$ in ether + dil H_2SO_4 Halogenoalkane + NH_3 in ethanol	 Amine Amine Amine + NH_4X
Reaction with halogenoalkanes	Amine (primary) + halogenoalkane (It is a **nucleophilic substitution** reaction.)	Secondary /tertiary amine or quaternary ammonium salt
Reaction with acyl chlorides	Amine + acyl chloride	N-substituted amide + HCl
Preparation of aryl amines (Reduction of aromatic nitro-compounds) - This reaction is used to produce phenylamine. Check the preparation of phenylamine for the details of this reaction.		

Hydrogenation of nitriles

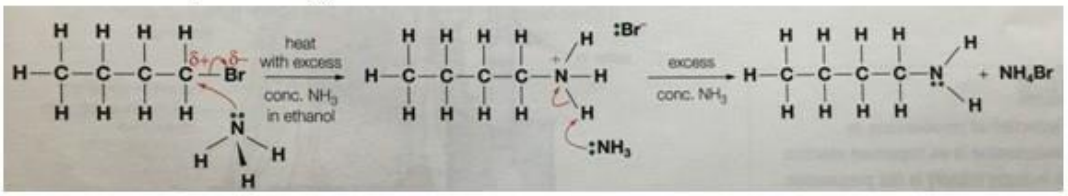
$$CH_3CH_2CH_2C{\equiv}N + 2H_2 \rightarrow CH_3CH_2CH_2CH_2NH_2$$

butanenitrile — butylamine

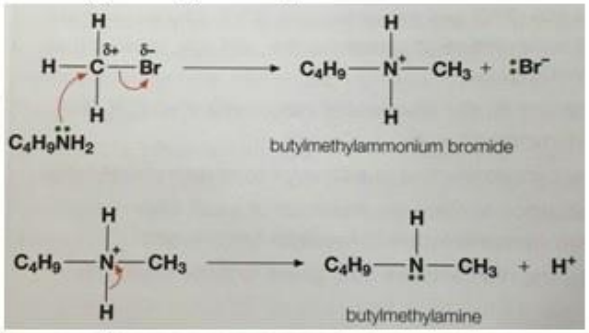
Nitrile + $LiAlH_4$ in ether + dil H_2SO_4

$$CH_3CH_2CH_2C{\equiv}N + 4[H] \rightarrow CH_3CH_2CH_2CH_2NH_2$$

Reaction of NH_3 and halogenoalkanes



Amine (primary) + halogenoalkane



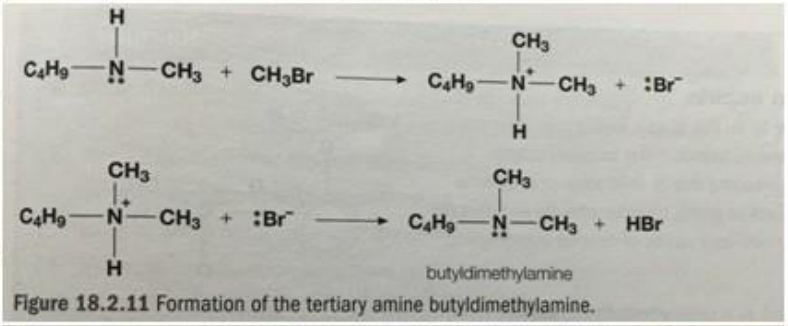
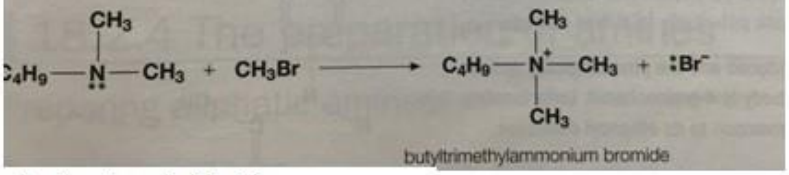
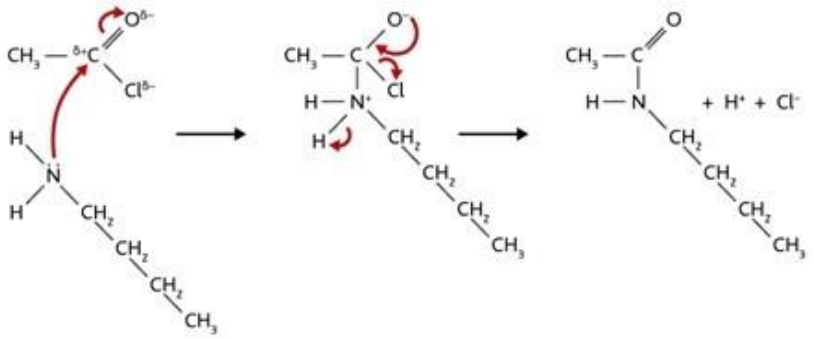


Figure 18.2.11 Formation of the tertiary amine butyldimethylamine.

The tertiary amine similarly can react further to form a **quaternary ammonium salt** (Figure 18.2.12).



Amine + acyl chloride



➔ Phenylamine

Preparation of phenylamine by reduction of aromatic nitro-compounds

Benzene and other aromatic compounds can be nitrated to form a nitro-compounds using a mixture of concentrated nitric acid and concentrated sulfuric acid. These nitro-compounds can produce aromatic amines.

Phenylamine can be produced by reduction of nitrobenzene using a mixture of tin and concentrated hydrochloric acid:

Tin reacts with concentrated hydrochloric acid to produce tin(II) ions and hydrogen:

$$Sn(s) + 2HCl(aq) \rightarrow Sn^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$$

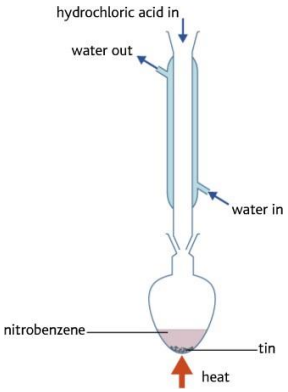
The tin(II) ions are oxidised to tin(IV) ions and these reduce the $-NO_2$ group to the $-NH_2$ group:

$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^{-}$$

$$C_6H_5NO_2(l) + 6H^{+}(aq) + 6e^{-} \rightarrow C_6H_5NH_2(l) + 2H_2O(l)$$

The flask is then cooled and sodium hydroxide solution is added to redissolve the initial precipitate of tin(IV) hydroxide, $Sn(OH)_4$ – tin(VI) hydroxide is amphoteric and with excess alkali produces the soluble $Sn(OH)_6^{2-}$ ion.

Water is then added and steam distillation is used to separate the mixture of phenylamine and water. The distillate initially collected is cloudy because it is an emulsion of phenylamine and water. When the distillate is clear, only water is distilling over.



Powdered sodium chloride is added to the distillate and the mixture is transferred to a separating funnel. This is shaken well – phenylamine is significantly soluble in water, but very much less so in saturated sodium chloride solution. This process is called salting out.

The mixture is then transferred to a separating funnel and ethoxyethane is added and shaken, relieving the pressure in the separating funnel occasionally by opening the tap. The layers are allowed to separate, and then lower aqueous layer is run off into a small beaker.

The ethoxyethane layer is transferred to a small conical flask, and further extraction of the aqueous layer with further portions of ethoxyethane is carried out. The ethoxyethane extracts are combined – this is an example of solvent extraction.

Pellets of potassium hydroxide are added to dry the ethoxyethane extract. Potassium hydroxide is better than calcium chloride or anhydrous sodium sulfate because, being alkaline, it will remove any traces of hydrochloric acid.

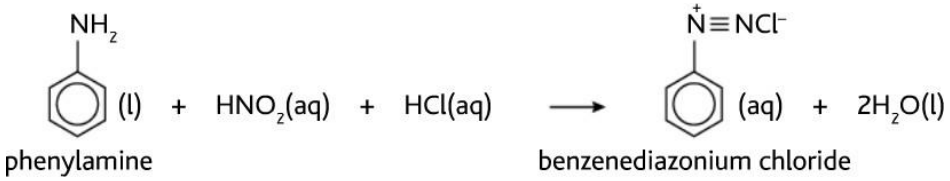
The ethoxyethane is distilled off and finally phenylamine is distilled off, collecting the fraction between 180 and 185°C.

➔ Diazonium compounds and their reactions

Aromatic amines, such as phenylamine, can be converted into diazonium salts by reaction with nitrous acid HNO_2. Nitrous acid is a very unstable compound which exists only in aqueous solution and decomposes at room temperature. The nitrous acid must be prepared as needed in situ by mixing ice-cold solutions of sodium nitrate and dilute hydrochloric acid:

$$NaNO_2(aq) + HCl(aq) \rightarrow NaCl(aq) + HNO_2(aq)$$

Nitrous acid is reacted with phenylamine at a temperature of less than 5°C.

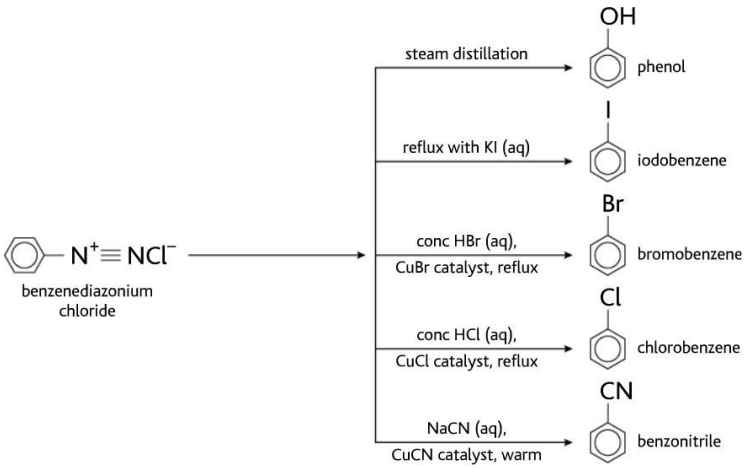


Diazonium compounds are generally very unstable at room temperature. If aliphatic amines are used, diazonium salts are not produced because they are so unstable – they decompose almost immediately as they are formed, even at a very low temperature. Aromatic diazonium salts, such as benzenediazonium chloride, are more stable, at least up to 10°C or so. This **additional stability results from the delocalised electrons of the benzene ring**.

The high activity of diazonium salts can be put to use in a wide variety of situations in organic synthesis procedures. The use of diazonium ions is based on two aspects of their chemistry – attack of the diazonium benzene ring by nucleophiles, and the ability of diazonium salts to couple with other molecules. When nucleophiles react with the benzene ring, nitrogen gas is evolved – this does not happen when diazonium ions couple with other molecules.

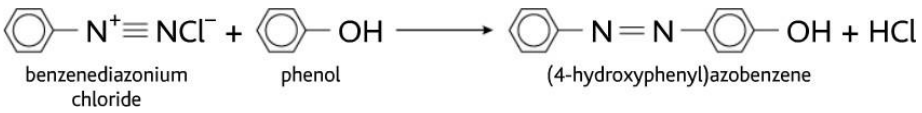
Diazonium compound reactions with nucleophiles

The diazonium group opens the benzene ring to attack by nucleophiles, such as amines. Nitrogen gas is evolved in these reactions.



Diazonium compound reactions as electrophiles

The benzenediazonium ion caries a positive charge and so is a strong electrophile. It reacts readily in cold alkaline solution both with aromatic amines an with phenols – they attack giving brightly coloured diazo-compounds. These reactions, joining two aromatic rings together, are known as coupling reactions. In coupling reactions, no nitrogen gas is produced.



The diazo-compounds produced are complex molecules with a minimum of two aromatic rings joined by an $N \equiv N$ coupling. Unlike the diazonium compounds from which they are made, di-azo compounds are extremely stable and unreactive. The bright colours they have are the result of the extensive delocalised electron systems that spread across the entire molecule through the $N \equiv N$ coupling.

The aromatic rings are joined together through the azo group (– N = N –). These dyes cam absorb light in the visible part of the spectrum.

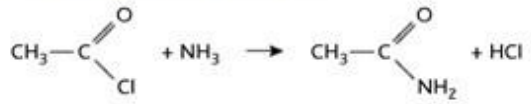
L-) Amides

Amides are carboxylic acid derivatives.

- **Reactions of amides**

Reaction	Products
Preparation of amides: Conc NH_3 + acyl chloride Amine + acyl chloride	 Amide + HCl N-substituted amine + HCl
Addition polymerisation using: 2-propeneamide	 Poly(propenamide)
Trans-esterification reaction: Poly(ethenyl ethanoate) + methanol	 Poly(ethenol)
Condensation polymerisation: Hexanedioic acid + 1,6-diaminohexane Benzene-1,4-dioic acid + benzene-1,4-diamine	 Nylon 6,6 + H_2O Kevlar + H_2O

Conc NH_3 + acyl chloride



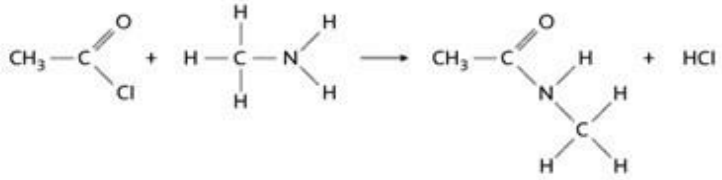
ethanoyl chloride ethanamide

fig. 1.6.75 Reaction of acyl chlorides with ammonia.

Because of the acid/base nature of the products, a further reaction takes place:

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

Amine + acyl chloride

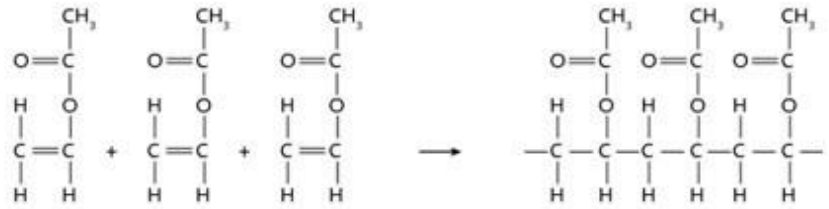


methylamine *N*-methylethanamide

2-propeneamide

2-propenamide poly(propenamide)

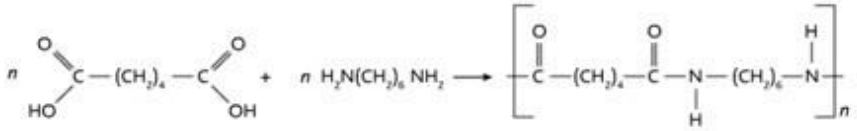
Poly(ethenyl ethanoate) + methanol



ethenyl ethanoate poly(ethenyl ethanoate)

poly(ethenyl ethanoate) poly(ethenol)

Hexanedioic acid + 1,6-diaminohexane



hexanedioic acid 1, 6-diaminohexane nylon 6,6

Benzene-1,4-dioic acid + benzene-1,4-diamine

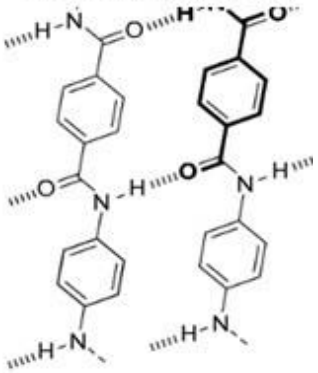


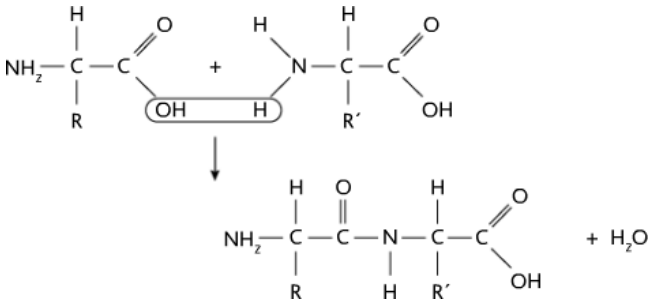
fig. 2.4.20 The structure of Kevlar: it consists of long polymer chains of paraphenylene terephthalamide – sometimes called para-aramid fibres – with strong hydrogen bonds between the chains.

M-) Amino acids

Amino acids are organic compounds containing an amide and a carboxylic acid group.

The peptide group – condensation reaction

When two amino acids join together, they undergo a condensation reaction and lose a molecule of water. The resulting bond is a peptide bond and the molecule is called a dipeptide.

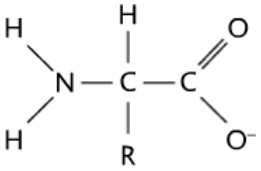


Chains of many peptide groups form polypeptides which fold to form the proteins.

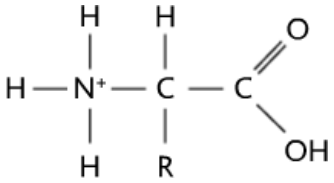
Acidic and basic properties of amino acids

Amino acids have interesting properties because they contain both an acidic group and a basic group.

In an alkaline solution, the amino acid loses a proton and forms a negative ion:

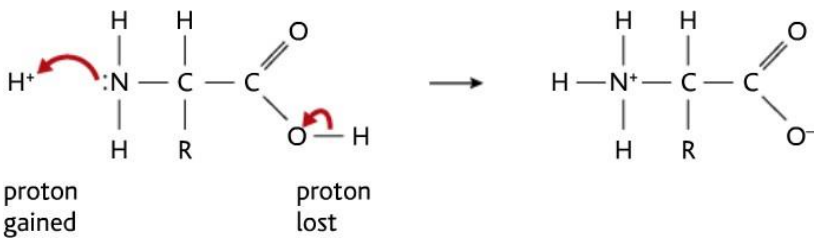


In an acidic solution, the molecule receives a proton and forms a positive ion:



In a neutral solution, amino acids exist with both the positive and negative ions within the same molecule. This species is called a zwitterion.

Amino acids can exist as zwitterions when in the solid state. This explains their relatively high melting temperature when compared with similar compounds and why they dissolve in water. Amino acids do not dissolve in organic solvents.



Tests for functional groups

- **Alkenes (C=C)**

  i) Reaction with bromine water (electrophilic addition)

  Shake 1 cm^3 of the compound with 1 cm^3 of bromine water (or bubble it through if a gas) in the dark. If the orange bromine is decolourised, this confirms an alkene

  e.g. $H_2C{=}CH_2 + Br_2 \longrightarrow Br{-}CH_2{-}CH_2{-}Br$

  ii) Reaction with acidified potassium manganate(VII) (oxidative addition)

  Shake 1 cm^3 of the compound with 1 cm^3 of potassium manganate(VII) solution acidified with a little dilute sulphuric acid (or bubble it through if a gas). If the purple manganate(VII) is decolourised, this confirms an alkene

  e.g. $H_2C{=}CH_2 + [O] + H_2O \xrightarrow{KMnO_4,\ H^+/\ OH^-} HO{-}H_2C{-}CH_2{-}OH$

- **Halogenoalkanes (R-X)**

  Reaction with aqueous sodium hydroxide (nucleophilic substitution)

  Add 1 cm^3 of the compound to 1 cm^3 of aqueous sodium hydroxide in a test tube and heat to 50ºC in a water bath; neutralise excess hydroxide with dilute nitric acid; add 1 cm^3 of aqueous silver nitrate

  White ppt of AgCl ⇒ R-Cl; cream ppt of AgBr ⇒ R-Br; yellow ppt of AgI ⇒ R-I

  e.g. $R\text{-}X + OH^- \xrightarrow[\text{warm}]{\text{aqueous KOH}} R{-}OH + X^-$

- **Alcohols (R-OH)**

  Reaction with phosphorus pentachloride

  Add a spatula measure of PCl_5 solid to 1 cm^3 of the liquid to be tested. An exothermic reaction which evolves steamy fumes (HCl) which turn damp litmus red and form a white 'smoke' with ammonia gas confirms the presence of an –OH group in the molecule. As this also gives a positive result with water (H-OH) and carboxylic acids (RCOOH), you must also be sure that the 'unknown' is dry and neutral before you can confirm it is an alcohol

  e.g. $R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$

Once you have confirmed an alcohol is present, you may need to identify it as primary, secondary or tertiary

a) Primary alcohols ($R{-}CH_2{-}OH$)

Oxidise with potassium dichromate acidified with a little dilute sulphuric acid, distilling off the product. If the product shows a positive test for an aldehyde (see below) the 'unknown' must be a primary alcohol

e.g. $R{-}CH_2{-}OH + [O] \xrightarrow[\text{distil off product}]{K_2Cr_2O_7,\ H^+} R{-}\overset{\overset{O}{\parallel}}{C}{-}H + H_2O$

b) Secondary alcohols ($R_2CH{-}OH$)

Oxidise with potassium dichromate acidified with a little dilute sulphuric acid, distilling off the product. If the product shows a positive test for a carbonyl group but a negative test for an aldehyde (see below) the product must be a ketone and the 'unknown' must be a secondary alcohol

e.g. $R_2CH{-}OH + [O] \xrightarrow[\text{distil off product}]{K_2Cr_2O_7,\ H^+} R{-}\overset{\overset{O}{\parallel}}{C}{-}R + H_2O$

c) Tertiary alcohols ($R_3C{-}OH$)

Attempt to oxidise by warming with potassium dichromate acidified with a little dilute sulphuric acid. If the potassium dichromate remains orange, no oxidation has taken place and the 'unknown' must be a tertiary alcohol

e.g. $R_3C{-}OH + [O] \xrightarrow{K_2Cr_2O_7,\ H^+}$ no reaction

d) Compounds containing $-CH(CH_3)OH$ – the iodoform (triiodomethane) reaction

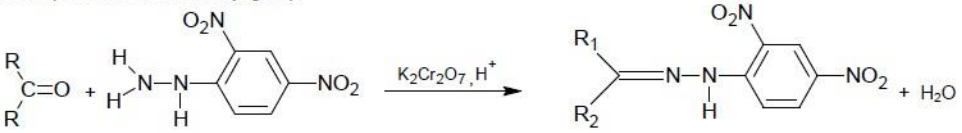
To 2 cm^3 of aqueous sodium hydroxide add 1 cm^3 of the 'unknown' followed by a few drops of iodine solution, stopper and shake well. The production of a pale yellow crystalline precipitate (of triiodomethane) confirms the presence of either the $-CH(CH_3)OH$ group (present in secondary methyl alcohols or ethanol) **or** a methyl ketone (see below) which must be distinguished by additional tests.

e.g. $RCH(CH_3)OH + 6\ OH^- + 4\ I_2 \longrightarrow CHI_3 + RCOO^- + 5\ I^- + 5\ H_2O$

- **Carbonyl compounds ($R_2C{=}O$)**

  Reaction with 2,4-dinitrophenylhydrazine (condensation)

  Add a few drops of the 'unknown' to 1cm^3 of a solution of 2,4-DNP in methanol. A dense yellow or orange precipitate confirms the presence of a carbonyl group

e.g. 

Once a carbonyl group has been identified, it may be confirmed as either an aldehyde or ketone by one of the following procedures:

a) Aldehydes (RCHO)

Aldehydes are reducing agents; they may be oxidised to carboxylic acids (in acidic solution) or their salts (in alkaline solution). Positive tests for aldehydes (i.e. to distinguish them from ketones) depend on this fact.

i) Acidified potassium dichromate

Add 1 cm^3 of dilute sulphuric acid to 1 cm^3 of potassium dichromate solution. Add 1 cm^3 of the 'unknown' and heat to 50 ºC in a water bath. If the colour changes from orange to green, the dichromate(VI) has been reduced to chromium(III) and an aldehyde is confirmed.

e.g. $3\ RCHO + Cr_2O_7^{2-} + 8\ H^+ \xrightarrow{\text{heat}} 3\ RCOOH + 2\ Cr^{3+} + 4\ H_2O$

ii) Tollens' reagent (silver mirror test)

Add a few drops of aqueous sodium hydroxide to 1 cm^3 of silver nitrate solution to produce a precipitate of silver oxide. Add just enough aqueous ammonia to redissolve this precipitate and form a colourless solution. Add 1 cm^3 of the 'unknown' and heat in a water bath at 50 ºC for a few minutes. If a 'silver mirror' is formed on the inside of the test tube, this confirms the presence of an aldehyde.

e.g. $RCHO + 2\ Ag(NH_3)_2^+ + 3\ OH^- \xrightarrow{\text{heat}} RCOO^- + Ag + 4\ NH_3 + 2\ H_2O$

iii) Fehling's (or Benedict's) solution

Both Fehling's and Benedict's solutions contain complexed copper(II) ions in an alkaline solution.
To 1 cm^3 of freshly prepared Fehling's (or Benedict's) solution add 1 cm^3 of the 'unknown' and heat in a water bath at 50 ºC for a few minutes. If a red precipitate of copper(I) oxide is formed, this confirms the presence of an aldehyde.

e.g. $RCHO + 2\ Cu(L\text{-}L)_2^{2+} + 5\ OH^- \xrightarrow{\text{heat}} RCOO^- + Cu_2O + L\text{-}L + 3\ H_2O$

b) Ketones (R_2CO)

Ketones are not reducing agents; they may not be oxidised to carboxylic acids. If a carbonyl compound gives negative results with any of the tests above it confirms the presence of a ketone.

i) Methyl ketones ($RCOCH_3$) – the iodoform (triiodomethane) reaction

Methyl ketones undergo the iodoform reaction (for experimental details see methyl secondary alcohols). The production of a pale yellow crystalline precipitate confirms the presence of a methyl secondary alcohol **or** a methyl ketone (which must be distinguished by additional tests).

e.g. $RCOCH_3 + 4\ OH^- + 3\ I_2 \longrightarrow CHI_3 + RCOO^- + 3\ I^- + 3\ H_2O$

- ## Carboxylic acids (RCOOH)

There is **no single test** for a carboxylic acid, but they may be confirmed by a combination of tests

i) Reaction with phosphorus pentachloride

Carboxylic acids contain a hydroxyl (-OH) group. They therefore react with PCl_5 in the same manner as described for alcohols above

ii) Reaction with water

Carboxylic acids are weak acids, i.e. they are only partially ionised in aqueous solution. Most are reasonably soluble, giving a solution with a pH in the range 3-5. Some long-chain carboxylic acids may be only sparingly soluble, giving a solution with a pH only marginally below 7.

e.g. $RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$

iii) Reaction with sodium carbonate (or hydrogencarbonate)

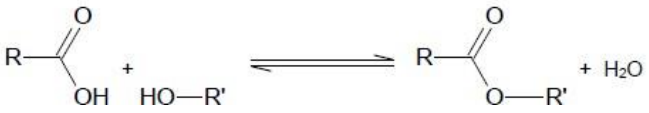
Carboxylic acids are weak acids, but generally acidic enough to react with both sodium carbonate and sodium hydrogencarbonate to produce carbon dioxide gas. So, add 1cm^3 of the 'unknown' to 1 cm^3 of sodium carbonate solution (or a spatula measure of the solid). If effervescence occurs, collect a sample of the gas in a disposable pipette and bubble through 1 cm^3 of lime water. If the lime water turns cloudy this confirms CO_2 has been evolved and the 'unknown' is an acid. This distinguishes carboxylic acids from weaker acids, such as phenol, which do not react with sodium carbonate.

e.g. $2\ RCOOH + Na_2CO_3 \longrightarrow 2\ RCOO^-\ Na^+ + CO_2 + H_2O$

iv) Reaction with an alcohol (esterification)

To 1 cm^3 of ethanol in a test tube add 1 cm^3 of the 'unknown' followed by a few drops of concentrated sulphuric acid (catalyst). Heat to 50 ºC in a water bath for five minutes. Pour the product into a beaker containing 20 cm^3 of sodium carbonate solution (to neutralise any excess acid). If the product smells of 'glue' or 'pear drops' an ester has been formed and the 'unknown' is confirmed as a carboxylic acid.

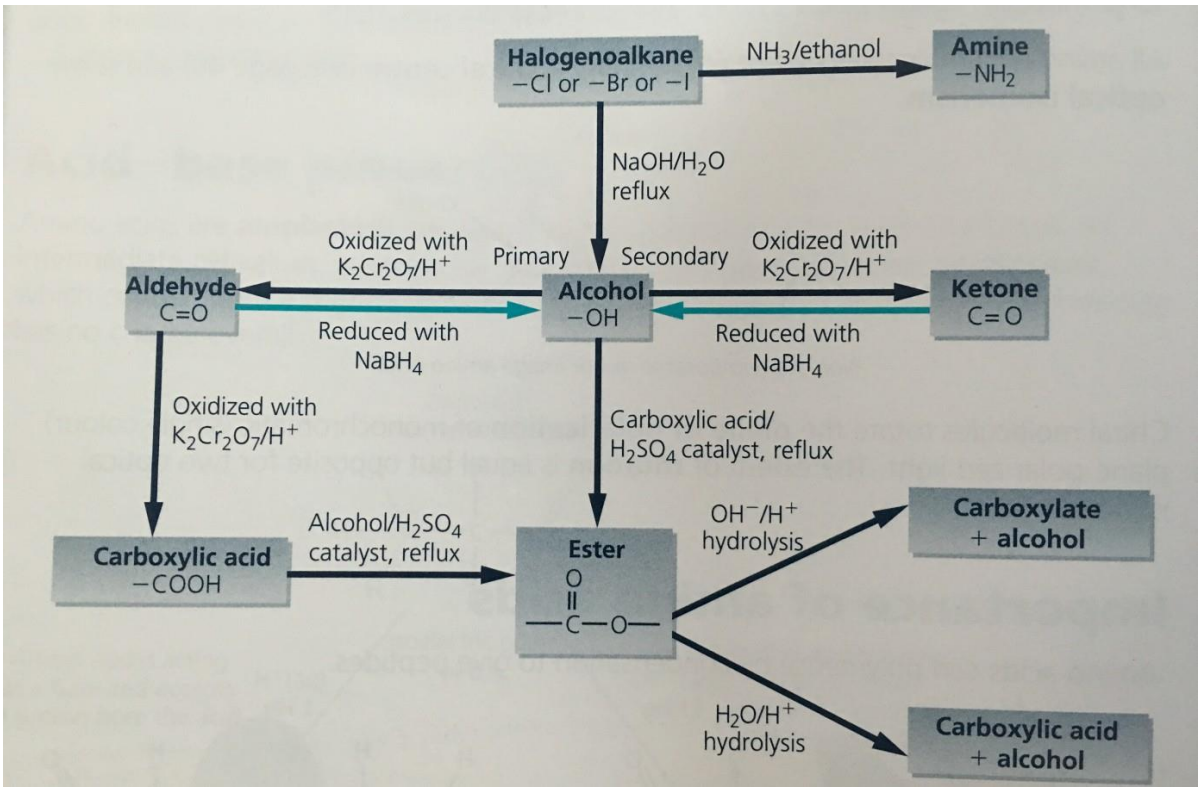
e.g.



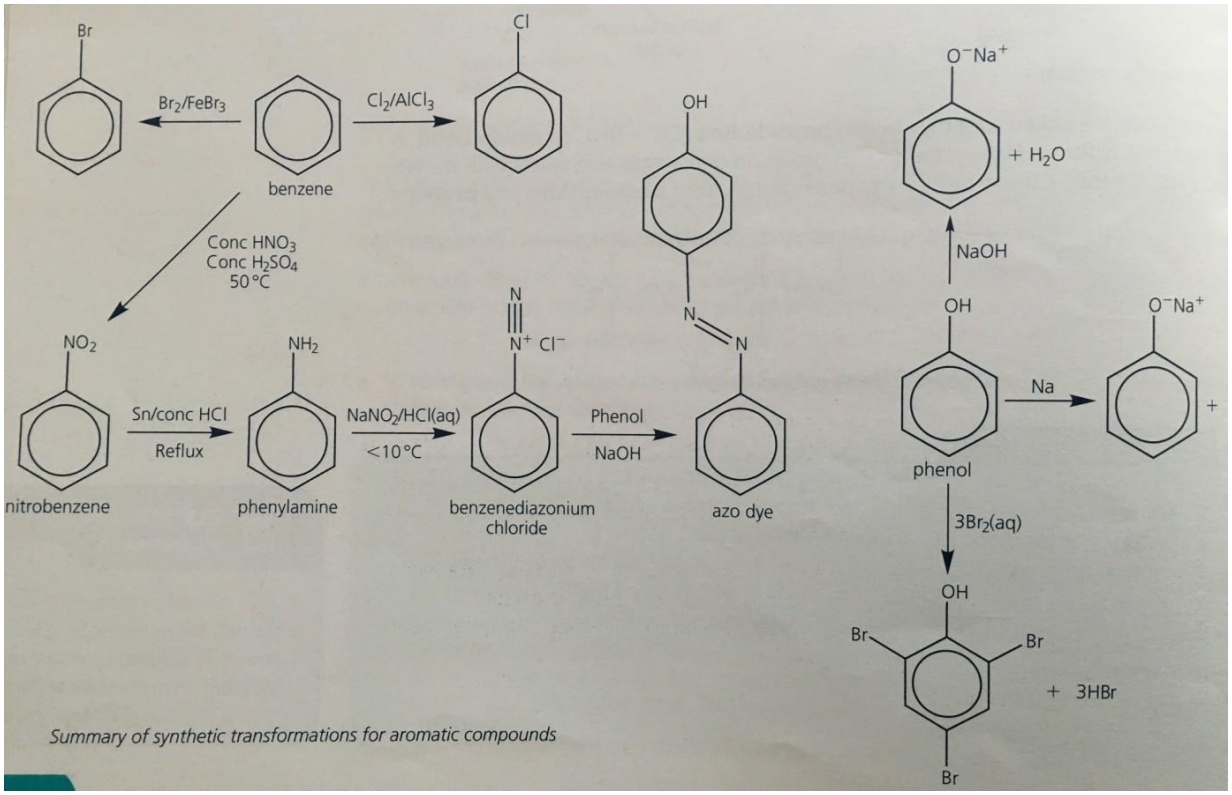
ORGANIC SYNTHESIS

Organic synthesis is a way of modifying existing molecules, or assembling new ones, to give useful products – for example paracetamol, dyes and polymers.

A. SUMMARY OF SYNTHETIC TRANSFORMATIONS FOR ALIPHATIC CARBON COMPOUNDS



B. SUMMARY OF SYNTHETIC TRANSFORMATIONS FOR AROMATIC COMPOUNDS



Summary of synthetic transformations for aromatic compounds

Adding or removing a carbon atom from an organic molecule

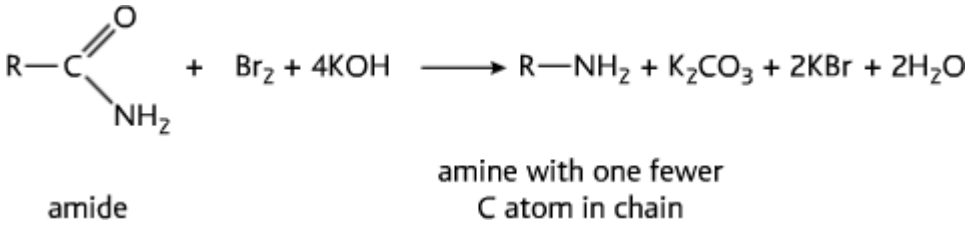
To add a carbon atom to a chain, start with halogenoalkane and reflux it with potassium cyanide dissolved in ethanol. This will produce a nitrile. Hydrolysis of the nitrile by refluxing with dilute hydrochloric acid (or sodium hydroxide followed by acidification) produces the carboxylic acid:

$$\underset{\text{halogenoalkane}}{R{-}X} + KCN \longrightarrow \underset{\text{nitrile with extra C atom in chain}}{RCN} + KX$$

$$\underset{\text{nitrile}}{RCN} + 2H_2O \longrightarrow \underset{\text{carboxylic acid}}{RCOOH} + NH_3$$

Friedel-Crafts alkylation reactions provide another means of adding one or more carbon atoms to an aromatic molecule.

Reducing the number of carbon atoms in a chain can be done by Hofmann's degradation in which an amide is heated with bromine and concentrated potassium hydroxide:



Another way of reducing the length of a carbon chain is by the Hunsdiecker reaction. If the silver salts of carboxylic acids are reacted with halogens such as bromine then an organic halide, carbon dioxide and an inorganic silver salt will result. The reaction is carried out under reflux in tetrachloromethane.

$$\text{RCOOAg(aq)} + \text{Br}_2\text{(l)} \xrightarrow{\text{reflux in } \text{CCl}_4} \text{RBr(l)} + \text{CO}_2\text{(g)} + \text{AgBr(s)}$$

The organic halide has a reduced number of carbon atoms in the skeleton, and can be used in further synthetic steps.

C. Importance of Analysis

At each stage of organic synthesis, the identity of the product can be checked using analytical techniques. Other benefits include:

- Monitoring reaction progress (extent of a reaction) – reaction conditions may then be modified to improve yields
- Identifying unreacted starting materials or unwanted by-products that must be removed.

The technique must be sensitive enough to determine structure, even when only tiny quantities are available as with many natural products when first obtained from plants and animals.

D. Deductions Based on Analytical Data

The empirical formula of an unknown compound is found from:

- Combustion analysis: a sample is burnt in excess oxygen and the products (CO_2 and H_2O) are absorbed and measured giving the percentage composition of carbon and hydrogen
- The percentage composition by element

Molecular and structural formula can then be deduced by combining this data with:

- Characteristic reactions of functional groups
- Mass spectrometry: data to determine the relative molecular mass – fragmentation patterns may indicate possible structures
- Infrared spectrometry
- Nuclear magnetic resonance (nmr)

E. HAZARD AND RISK IN ORGANIC SYNTHESIS

Hazard: The hazard presented by a substance or activity is its potential to do harm. This potential is absolute.

Risk: The risk associated with a particular hazard is the chance that it will actually cause harm. Risk is affected by a number of things, in particular the nature of the hazard involved and the level of exposure. A hazardous substance can be safe to use if the risks are minimised.

Risk assessment with organic compounds

There are a number of hazard particularly associated with organic chemicals. Many of these chemicals are poisonous and/or carcinogenic. Many are flammable. As a result, when working with organic chemicals it is very important to carry out the full risk assessment. The purpose of this is to identify the risks of using hazardous chemicals and reduce them as far as possible.

Ways of reducing risk

1-) Working on a smaller scale

- There is less risk of inhaling fumes with smaller amounts of chemicals because there are less fumes.
- If heat is given out, this will be less for smaller quantities of reactants.
- Smaller quantities are easier to transfer from one container to another without spillage.

2-) Safety precautions

- Wearing safety goggles, gloves and lab coat when dealing with irritant or corrosive liquids.
- Use of a fume cupboard – so any harmful gases are vented from the laboratory.

3-) Using alternative methods with less hazardous substances

F. CHIRAL SYNTHESIS

Many drug compounds are chiral but only one of the isomers may have a beneficial medical use. The other may even have harmful effects.

To avoid producing the unwanted isomer, chiral synthesis is used to make stereospecific drugs with a single optical isomer. The natural compound is always produced as single optical isomer – chiral synthesis may use enzymes that are stereospecific. Knowing the mechanism of the reaction can help to plan a synthesis to produce a single optical isomer.

G. COMBINATORIAL CHEMISTRY

A pharmaceutical company may need to synthesise and test a million compounds before locating a few hundred useful ones.

Combinatorial synthesis is an automated process widely used in the pharmaceutical industry to produce large numbers of related compounds similar to an existing drug. Using a specific synthetic route, a set of starting materials is automatically combine in slightly different ways.

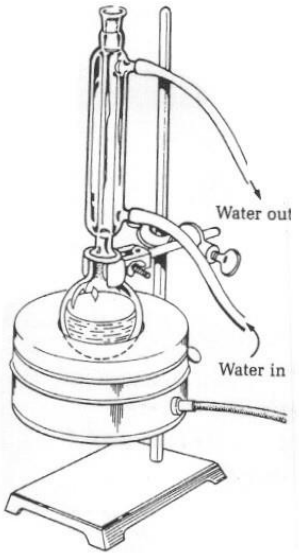
A solid polymeric support, often beads, helps to automate the process. The polymer is inert but has a suitable functional group attached to it. This linker group bonds to a reagent passing over the beads, and to successive reagents at each stage in the synthesis. Excess reagents and their by-products wash away, leaving the product immobilised on the beads. Care is taken to maximise the yield at each stage of the synthesis.

ORGANIC SYNTHESIS TECHNIQUES

A. REFLUXING

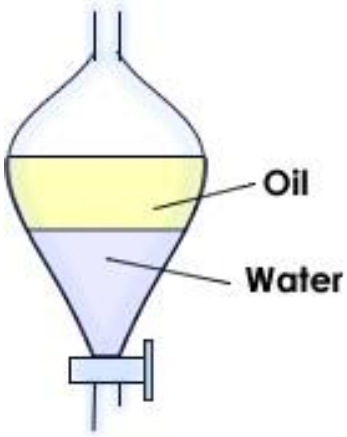
Heating under reflux is necessary when the reactant is volatile and the reaction is slow at room temperature.

Heating in a flask with a reflux condenser prevents vapours escaping while the reaction is happening. Vapours from the reaction mixture condense and flow back (reflux) into the flask.



B. Purification by Washing

Washing with sodium carbonate solution removes acid from a mixture of water and an insoluble compound. This is carried out by shaking with sodium carbonate solution in a separating funnel, followed by washing with water. Pure water removes any inorganic impurities.



C. Solvent Extraction

Solid or liquid products can be separated from an aqueous reaction mixture using the technique of solvent extraction. **The aqueous mixture is shaken in a separating funnel with a solvent which is immiscible with water.** The organic product dissolves preferentially in the organic layer, which in most cases is the upper layer. The lower aqueous layer can be drained off and the organic product can be obtained from the upper layer by evaporation of the solvent.

D. Recrystallisation

1) Dissolve the impure solid in the minimum volume of hot solvent to make sure the solution is saturated.
2) If the solution is not clear, filter the hot mixture through a heated funnel to remove any insoluble impurities.
3) Cool the filtrate so that the product recrystallises, leaving the smaller amounts of insoluble impurities in solution.
4) Filter to recover the purified product.
5) Wash the purified solid with small amounts of cold, pure solvent to wash away any solution containing impurities.
6) Allow the solvent to evaporate from the purified solid in the air or place the solid in a desiccator.

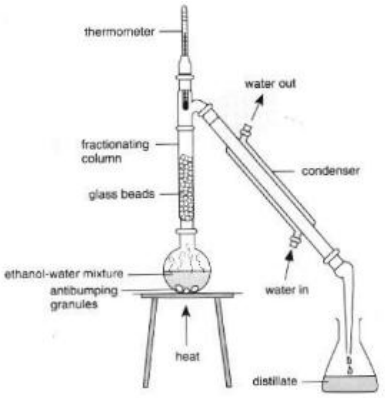
E. Drying

An organic liquid is dried using a solid drying agent such as pieces of anhydrous calcium chloride or anhydrous magnesium sulfate. The organic liquid, left to stand in contact with the solid, goes clear when any water present has been removed.

A solid can be dried by placing it in a desiccator.

F. DISTILLATION

Fractional distillation



Fractional distillation separates mixtures of liquids with different boiling temperatures. The process takes place in the distillation apparatus that has been fitted with a fractionating column between the flask and the still-head. Separation is improved if the column is packed with inner beads or rings to increase the surface area where rising vapour can mix with condensed liquid running back to the flask. The column is hotter at the bottom and cooler at the top. The thermometer
reads the boiling temperature of the compound passing over into the condenser.

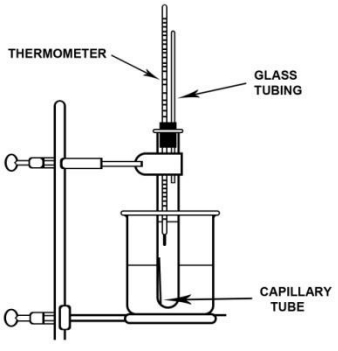
If the flask contains a mixture of liquids, the boiling liquid in the flask produces a vapour that is richer in the most volatile of the liquids present. Most of the vapour condenses in the column and runs back. As it does so, it meets more of the rising vapour. Some of the vapour condenses. Some of the liquid evaporates. Every time the vapour is richer in the most volatile liquid present. So, during fractional distillation, the most volatile liquid with the lowest boiling temperature distils first, then the liquid with the next lowest boiling temperature, and so on.

Steam distillation

Distillation with steam at 100° C allows the separation of compounds that decompose if heated at their boiling temperatures. The technique works only with compounds that do not mix with water. When used to separate the products of organic preparations, steam distillation leaves behind those reagents and products that are soluble in water. Steam is blown into the mixture and the oil and water distil off, leaving behind the solids.

G. MELTING AND BOILING TEMPERATURE DETERMINATION

Pure solids have sharp melting temperatures, but impure solids soften and melt over a range of temperatures. So watching a solid melt can often show whether or not it is pure. As databases now include the melting temperatures of all known compounds, it is possible to check the identity and purity of a product by



checking that it melts sharply at the expected temperature.

Like melting temperatures for solids, boiling temperatures can be used to check the purity and identity of liquids. If a liquid is pure it will all distil at the expected boiling temperature or in a narrow range including it. The boiling temperature can be measured as the liquid distils over during fractional distillation.

Unit AS 1: Basic Concepts in Physical and Inorganic Chemistry

N.B. It should be noted that the exact colour of a solution often depends on the concentration and the following are based on solutions of normal laboratory concentration.

The following are used as standard conventions throughout this document:

1. A forward slash (/) indicates each alternative will be accepted e.g. the sodium flame colour is given as yellow/orange so either yellow or orange will be accepted.

2. A hyphen (-) indicates that both colours are required e.g. bromine liquid is described as red-brown so red or brown will not be accepted.

3. Make a solution means dissolve in water.

Content	Paragraph	Observation	
1.2 Atomic structure	1.2.16	**Flame colours:**	
		Li^+	Crimson
		Na^+	Yellow/Orange
		K^+	Lilac/Pink through cobalt glass
		Ca^{2+}	Brick red
		Ba^{2+}	Green
		Cu^{2+}	Green-blue/Blue-green
1.8 Group VII (fluorine, chlorine, bromine and iodine	1.8.1	Fluorine	Yellow gas
		Chlorine	Green/Yellow-green/Green-yellow gas
		Bromine	Red-brown liquid (and vapour)
		Iodine solid	Grey-black/Black
		Iodine vapour	Violet/Purple
	1.8.2/1.8.6	Chlorine water	pale green/colourless
		Bromine water	yellow/orange/brown
		Iodine solution solvents	yellow/brown: polar violet/purple: non-polar solvents
	1.8.7	Iron (II) solution	pale green
		Iron (III) solution	yellow/orange
		Solid halides with concentrated sulphuric acid:	

		Fluoride	steamy/misty fumes (of HF)
		Chloride	steamy/misty fumes (of HCl)
		Bromide	steamy/misty fumes (of HBr); red-brown vapour (Br_2)
		Solid halides with concentrated sulphuric acid: (cont.)	
		Iodide	steamy/misty fumes (of HI); violet/purple vapour (I_2); smell of rotten eggs (H_2S); yellow solid (S); grey-black/black solid (on the sides of the test-tube) (I_2)
	1.8.11	Silver chloride	white
		Silver bromide	cream
		Silver iodide	yellow
1.9 Titrations	1.9.2	Methyl orange	Acid – red/pink Alkali – yellow
		Colour change at end-point:	
		adding acid to orange/red/pink alkali	yellow to
		adding alkali to orange/yellow acid	red/pink to
		Phenolphthalein	Acid – colourless Alkali – pink/red
		Colour change at end-point:	
		adding acid to colourless alkali	pink to
		adding alkali to pink acid	colourless to

Unit AS 2: Further Physical and Inorganic Chemistry and Introduction to Organic Chemistry

Content	Paragraph	Observation
2.12 Qualitative analysis	2.12.1	**Gas tests** H_2 gives a 'pop' with a burning splint O_2 relights a glowing splint Cl_2 bleaches damp litmus/universal indicator paper CO_2 bubble through limewater; limewater turns cloudy/milky SO_2 turns potassium dichromate (VI) solution from orange to green/turns potassium manganate (VII) solution form purple/pink to colourless HCl white fumes/smoke with stopper from bottle of concentrated ammonia solution/glass rod dipped in concentrated ammonia solution NH_3 white fumes/smoke with stopper from bottle of concentrated hydrochloric acid/glass rod dipped in concentrated hydrochloric acid
	2.12.2	**Flame colours** Li^+ Crimson Na^+ Yellow/Orange K^+ Lilac/Pink through cobalt glass Ca^{2+} Brick red Ba^{2+} Green Cu^{2+} Green-blue/Blue-green

	2.12.3	SO_4^{2-}	make a solution and add dilute HCl/HNO_3 followed by a solution of Ba^{2+} ions – forms a white precipitate
		HCO_3^-/CO_3^{2-}	add dilute HCl to form colourless gas which turns lime water cloudy/milky; make a solution and add a solution of Mg^{2+} ions – CO_3^{2-} forms a white precipitate, no effect on HCO_3^-
		Hal^-	make a solution and add dilute nitric acid followed by silver nitrate solution, then note the following:
		Cl^-	white precipitate, soluble in dilute ammonia solution
		Br^-	cream precipitate, soluble in concentrated ammonia solution
		I^-	yellow precipitate, insoluble in concentrated ammonia solution

	2.12.4	Ba^{2+}	yellow precipitate with a solution of potassium chromate, soluble in hydrochloric acid to give a yellow solution
		Cu^{2+}	blue precipitate on addition of a few drops of dilute ammonia solution which dissolves in excess of the ammonia solution to form a dark/deep blue solution
		NH_4^+	heat with dilute sodium hydroxide; the gas given off gives white fumes/smoke with stopper from bottle of concentrated hydrochloric acid/glass rod dipped in concentrated hydrochloric acid
		Fe^{2+} and Fe^{3+}	add dilute sodium hydroxide solution; Fe^{2+} gives a green precipitate and Fe^{3+} gives a rust/brown precipitate
		Al^{3+}, Mg^{2+} and dilute Zn^{2+} solution.	1. add a few drops of sodium hydroxide Al^{3+}, Mg^{2+} and Zn^{2+} all form a white precipitate. The Al^{3+} and Zn^{2+} precipitates are soluble in excess of the sodium hydroxide solution; the Mg^{2+} precipitate is insoluble in excess of the sodium hydroxide solution

			2. add a few drops of dilute ammonia solution. Al^{3+}, Mg^{2+} and Zn^{2+} all form a white precipitate. The Zn^{2+} precipitate is soluble in excess of the ammonia solution; the Al^{3+} and Mg^{2+} precipitates are insoluble in excess of the ammonia solution
		Fe^{3+}	add potassium thiocyanate solution and a blood red solution is formed

Unit A2 1: Periodic Trends and Further Organic, Physical and Inorganic Chemistry

Content	Paragraph	Observation
4.7 Aldehydes and ketones	4.7.8	Aldehydes and ketones form yellow/orange precipitates in the presence of 2,4-dinitrophenylhydrazine
	4.7.10	Aldehydes can be distinguished from ketones as they: turn acidified (potassium) dichromate solution from orange to green; form a red precipitate when heated with Fehling's solution; form a silver mirror when heated with Tollen's reagent

Unit A2 2: Analytical, Transition Metals, Electrochemistry and Further Organic Chemistry

Content	Paragraph	Observation
5.3 Volumetric analysis	5.3.1	**Recall the colour of the aqueous complexes of:** Ca^{2+}/Mg^{2+} using edta: eriochrome black T turns from red to blue I_2 with $S_2O_3^{2-}$ using starch: add the thiosulphate solution until the solution is straw coloured and then add starch; turns from blue-black to colourless Fe^{2+} with MnO_4^-: no indicator required the solution changes from colourless to pink
5.8 Oxidation states	5.8.1	**Recall the colour of the aqueous complexes of:** Cr^{3+} green Cr(VI) (CrO_4^{2-}) yellow $Cr_2O_7^{2-}$ orange Mn^{2+} pink Fe^{2+} green Fe^{3+} yellow/orange Co^{2+} pink Ni^{2+} green Cu^{2+} blue V^{2+} violet V^{3+} green V(IV) (VO^{2+}) blue V(V) (VO_2^+) yellow
	5.8.2	Qualitative detection tests using the formation of precipitates of the hydroxides with NaOH(aq) and NH_3(aq) and, where appropriate, their subsequent dissolution: Cr^{3+} green-blue precipitate soluble in excess sodium hydroxide solution Mn^{2+} white precipitate slowly turning brown/black on standing; insoluble in excess sodium hydroxide/ammonia solution Fe^{2+} green precipitate; insoluble in excess sodium hydroxide/ ammonia solution

		Fe^{3+}	rust/brown precipitate; insoluble in excess sodium hydroxide/ammonia solution

		Co^{2+}	blue precipitate; insoluble in excess sodium hydroxide solution; soluble in excess ammonia solution forming a yellow solution
		Ni^{2+}	green precipitate insoluble in excess sodium hydroxide solution; soluble in excess ammonia solution to form a blue solution
		Cu^{2+}	blue precipitate; insoluble in excess sodium hydroxide solution; soluble in excess ammonia solution to form a dark/deep blue solution
	5.8.3	V^{2+}	violet
		V^{3+}	green
		V(IV) VO^{2+})	blue
		V(V)(VO_2^+)	yellow
	5.8.5	Chrome alum	green solution; violet crystals